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Preremedial Design Report of Remediation Options for OU 7-13/14

Gretchen E. Matthern
Neal Yancey
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Peter Shaw

September 2005

Idaho Cleanup Project

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Gretchen E. Matthern
Neal Yancey
Gregory Hulet
Peter Shaw

Edited by Tasha Taylor and LauraLee Gourley

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Idaho Cleanup Project
Idaho Falls, Idaho 83415

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ABSTRACT

This report presents the results of tests determining the effectiveness of treatment options for radioactive mixed waste and makes recommendations for their use in remediating the Subsurface Disposal Area, a radioactive landfill that is part of the Radioactive Waste Management Complex at the Idaho National Laboratory. The treatment options—in situ thermal desorption, in situ grouting, and ex situ grouting—were tested using transuranic waste from the landfill and surrogate.

The testing provides additional data that will aid the U.S. Department of Energy in determining the effectiveness of these options as treatments for waste at the landfill. These data will be used in preparing the remedial investigation and feasibility study for Waste Area Group 7, Operable Unit 7-13/14, to help evaluate the safety, effectiveness, and risk of these alternatives considered for the feasibility study. Remediation is being performed under the Comprehensive Environmental Response, Compensation, and Liability Act.

EXECUTIVE SUMMARY

This report presents the results of testing based on the *Test Plan for the Evaluation of In Situ Thermal Desorption and Grouting Technologies for Operable Unit 7-13/14* (Yancey et al. 2003) and makes recommendations for consideration during ongoing development of the feasibility study for Operable Unit (OU) 7-13/14. When the test plan was being prepared, the three treatment options (in situ thermal desorption [ISTD], in situ grouting [ISG], and ex situ grouting [ESG]) included in it were being evaluated and were all under consideration for use in developing remedial alternatives for the feasibility study. Since the test plan was written, data gathered through the test plan evaluations, the *Second Addendum to the Work Plan for the OU 7-13/14 Waste Area Group 7 Comprehensive Remedial Investigation/Feasibility Study* (Holdren and Broomfield 2004), and the *Feasibility Study Preliminary Documented Safety Analysis for In Situ Thermal Desorption in the Subsurface Disposal Area* (Abbott 2003) have led to the elimination of ISTD as a treatment option for the feasibility study. The results, conclusions, and recommendations from ISTD testing are included in this report to document testing conducted as a part of the test plan.

Grouts under consideration for ISG—neat[a] and with various admixtures—were tested for (1) durability, (2) characteristics that tend toward leaching or binding of contaminants, and (3) data to support contaminant transport modeling for treated waste forms. For ISTD testing, major emissions were quantified as waste and soil were slowly heated to determine the degree of hazardous organic contaminant and nitrate removal or destruction from the test samples. These tests were guided by the *Test Plan for the Evaluation of In Situ Thermal Desorption and Grouting Technologies for Operable Unit 7-13/14* (Yancey et al. 2003).

This report provides additional data for the U.S. Department of Energy to aid in determining the effectiveness of ISG and ESG as treatments for waste at the Subsurface Disposal Area (SDA). Some of the data generated during these tests will support the remedial investigation and feasibility study for Waste Area Group 7 OU 7-13/14.[b] The SDA is being remediated under the Comprehensive Environmental Response, Compensation, and Liability Act (42 USC § 9601 et seq., 1980). The tests reported in this document address the Comprehensive Environmental Response, Compensation, and Liability Act criteria of effectiveness, both near and long term; reduction in mobility of contaminants through stabilization; and implementability. This document follows the organization and processes identified in guidance from the U.S. Environmental Protection Agency (EPA 1992).

In situ thermal desorption is commercially available and has been applied successfully at sites containing soil contaminated with organics (TerraTherm 2005a; Vinegar et al. 1998; Vinegar, Stegemeier, and Sheldon 1997); however, ISTD has not been demonstrated at sites containing buried containerized waste, radionuclides, nitrate salts, reactive mixtures, or large amounts of metal debris. The ISTD process under consideration uses electric resistance heaters to heat a region of the subsurface soil and waste to a prescribed temperature. Vapors generated by this heating process are collected and treated by an aboveground off-gas system. In situ thermal desorption can reduce the amount of contaminants in the subsurface by volatilization or, at higher temperatures, by degradation. Results from bench- and drum-scale tests and other evaluations (Abbott 2003) have shown that there are conditions where there is the potential to have uncontrolled reactions. In addition, there are conditions where ISTD may increase

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[a] Neat grout refers to any of the grout formulas that are used at 100% grout without waste or other additives. The neat grout was used as a baseline condition and compared with results when grouts were mixed with various waste loadings.

b. The *Federal Facility Agreement and Consent Order* (DOE-ID 1991) lists 10 WAGs for INL. Each WAG is subdivided into OUs. The RWMC is identified as WAG 7 and originally contained 14 OUs. Operable Unit 7-13 (TRU pits and trenches RI/FS) and OU 7-14 (WAG 7 comprehensive RI/FS) ultimately were combined into the OU 7-13/14 comprehensive RI/FS for WAG 7.

the mobility of some contaminants of concern. Because of these findings, ISTD is not recommended as a stand-alone treatment or a pretreatment for ISG at the SDA.

In situ grouting is being considered for treatment of transuranic (TRU) pits and trenches, and non-TRU pits and trenches and soil vault rows. Jet grouting is the specific ISG technique being considered for buried waste within the SDA. Jet grouting uses a specially designed rotary percussion drill rig to deliver and intimately mix grout with soil, debris, and contaminants in the subsurface. For purposes of this report, ISG will refer to jet grouting. The grout is injected at approximately 6,000 psi through small nozzles; high pressure combined with dense grout provides the energy required to mix the grout and subsurface materials. Each injection of grout in homogenous soil forms a column, and a series of diagonally offset columns forms a contiguous set of columns or monolith. Injection of grout in nonhomogenous waste can form columns with more variation in diameter, depending on voids and types of containers, but still interconnecting to form a monolith when a series of columns is placed in waste.

Grout must be designed specifically for ISG to meet the viscosity, particle size, and set times required for effective operation of the grouting rig. Past bench- and field-scale testing have demonstrated effectiveness and implementability of four of the grouts being tested. GMENT-12, U.S. Grout, TECT HG, and WAXFIX grout materials have been evaluated for leaching and physical characteristics to develop a recommendation of a single material for each application. Previous tests were conducted by Loomis et al. (2003) for application to TRU waste. The tests completed for this report were applicable to TRU, non-TRU, and Pad A waste. In addition to the proprietary grout formulations, five nonproprietary cementitious grout formulations (Portland cement, Portland cement with fly ash, Portland cement with slag, Portland cement with fly ash and thiosulfate, and Portland cement with slag and thiosulfate) were evaluated for immobilization of non-TRU radionuclides in soil. The primary component of each of these formulations, Portland cement, is the same as for GMENT-12, U.S. Grout, and TECT HG, making them viable alternatives for jet grouting; however, some additional tests would need to be conducted to verify that the nonproprietary grouts can be jet grouted and that they meet implementability criteria (Shaw 2004).

Ex situ grouting (solidification) is being considered for treatment of the Pad A salt waste. Ex situ grouting includes selection of an appropriate grout and an approach to transfer the waste from Pad A to a mixing system. This report examines only grout selection. Three candidate grouts[c] have been identified for testing as an ESG: Polysiloxane, Saltstone, and WAXFIX. Portland cement and other nonproprietary grouts generally do not handle high salt loads such as those that would be present in Pad A waste.

The tests in this report address six main objectives from Yancey et al. (2003):

- **Develop data to support contaminant transport modeling for treated waste forms.** Data obtained from these tests will be used in modeling migration of contaminants in the final waste form after ISG or ESG. In addition, these data will be used to determine changes in leachability of actinides from waste and surrounding soil following ISTD heating. These data will support modeling to estimate the release rate of contaminants from the treated waste and compare it to the predicted release rate from untreated waste. The test results also will support risk assessment, risk modeling, and performance evaluation portions of the feasibility study for OU 7-13/14.

c. Dimethyl Polysiloxane, marketed by Technology Visions Group, uses a polymer encapsulation technology (Loomis, Miller, and Prewett 1997) shown to successfully encapsulate surrogate salt materials. Saltstone grout, developed by Savannah River Site, has been developed for salt encapsulation. WAXFIX also is considered in the in situ portion of Yancey et al. (2003).

- **Evaluate durability of grouted waste.** Physical property data will be obtained to compare grouts and waste loadings. Long-term physical stability of the grouted waste forms will be estimated from these near-term tests.

- **Evaluate WAXFIX for use as a grout.** The purpose of these tests is to understand better the advantages and limitations of WAXFIX as a grout for TRU and non-TRU waste. Data will be used to address potential criticality and reactivity concerns that may be encountered with specific types and concentrations of contaminants. The ability of WAXFIX to contain radionuclides and nitrates is evaluated. In addition, the generation rate of hydrogen gas for WAXFIX mixed with radionuclides will be assessed because of the radiolysis process.

- **Quantify major emissions as waste and soil are slowly heated.** Determining primary off-gas constituents and concentrations as waste and soil are heated will help identify the off-gas processing requirements for full-scale test planning. The carbon monoxide and carbon dioxide releases determine the relative amounts of combustion and pyrolysis occurring. The gas proportion measurements also could assist in monitoring the type of waste being heated and any nitrate organic reactions. In addition, these data will support the generation of safety and design data for OU 7-13/14.

- **Determine the degree of hazardous organic contaminant and nitrate removal or destruction from soil and waste.** Quantifying the removal or destruction of chlorinated volatile organic compounds (VOCs) and nitrate salts in the waste will help establish anticipated efficiency of ISTD-mediated removal or destruction of contaminants of concern in TRU pits and trenches waste. Data also will be used to generate design data for the pending feasibility study for OU 7-13/14.

- **Test potential mixtures of organics and nitrates for reactivity.** Determining whether mixtures of nitrate salt sludge and organic sludge will react exothermically during heating by ISTD will help establish temperature ranges to avoid such reactions.

The ISTD testing raised, as well as answered, questions about applicability of ISTD to the SDA. Nitrate salts are expected to react exothermically with various forms of carbon in the waste. As shown most clearly in the thermal gravimetric analysis tests, the chemical form of carbon and rate of temperature increase of the system affect the magnitude and intensity of the reaction. The drum-scale reactivity experiments failed to demonstrate a method to heat nitrate salt surrogate and carbon-containing materials in a manner that maintained control over reaction between nitrate and carbon. Based on thermal gravimetric analysis and drum-scale results, it may be possible to heat mixtures of nitrate and carbon-containing waste in a manner that keeps the reaction under control, but it would require slow rates of heating and control of hot-spot formation. In a heterogeneous, uncharacterized waste form (i.e., containing organics and nitrates), such as exists in the SDA, the potential for uncontrolled exothermic reactions exist. Therefore, ISTD could not be implemented safely based on the results of the bench- and drum-scale tests.

In situ thermal desorption should be able to remove VOCs and oils from the subsurface through a combination of volatilization, oxidation, and reduction. The fate of radionuclides during ISTD cannot be conclusively stated based on data collected during this testing. Elimination of organic compounds and nitrate would simplify and improve the overall performance of grout in the waste; however, all of the grouts tested can tolerate the presence of some amount of organic and nitrate compounds. Elimination of only the VOCs would significantly reduce the inventory of chlorinated organic compounds, some of which are contaminants of concern, and would reduce by about half the total mass of organic compounds present in the waste. The removal of VOCs could likely be done at temperatures below 230°C (446°F) to avoid the nitrate-cellulose reaction, but additional testing and modeling would be required to demonstrate

the technical and economic feasibility of this approach. By reducing the total mass, grouting will work more effectively by increasing the amount of grout that can be injected into the waste, thus decreasing the waste-to-grout ratio; however, because of the potential for uncontrolled exothermic reactions and the potential to increase contaminant mobility in some cases, ISTD is not recommended at the SDA.

The ISG tests did not demonstrate one grout formulation to be significantly better than the other grout formulations for all radionuclides and waste forms evaluated. The waste loadings used in the leach tests were determined by the maximum amount of waste or surrogate that could be added to the grout and still maintain a cohesive sample. Although the leach index was expected to decrease as waste loading increased, this was not observed. For many of the samples containing TRU isotopes (i.e., uranium, americium, plutonium, and neptunium), the concentrations of radionuclides in the leachate were below the detection limit; therefore, the leach index was calculated from the detection limit. For the samples containing TRU isotopes, most of the leach indices (with the exception of neptunium) are greater than 10, indicating low effective diffusivity and high resistance to leaching. Because most data came back nondetectable, the leach indices did not vary much either.

Radionuclides were added at concentrations that were detectable in the untreated waste; therefore, all of the grouts were successful at reducing the leachability of the radionuclides tested. If the grout functions only as a macroencapsulation agent, then chemistry of the radionuclide is not important. If the grout immobilizes contaminants through a combination of chemical interaction and macroencapsulation, such as is the case with cementitious formulations, then chemistry of the contaminant is important. For this reason, the TRU radionuclides may behave differently from non-TRU radionuclides, with respect to leaching, when grouted in cementitious materials. The leach index values for all the radionuclides (TRU and non-TRU) were approximately the same in WAXFIX. This is not surprising since WAXFIX works by encapsulation of the contaminant. For all of the samples containing non-TRU isotopes (i.e., carbon, technetium, and iodine), concentrations of the radionuclides in the leachate were above detection limits. The leach index of non-TRU isotopes was generally lower than that for TRU isotopes in U.S. Grout and TECT HG. Cementitious grouts immobilize contaminants through a combination of chemical interaction and encapsulation. The difference seen between the two classes of radionuclides within the cementitious grouts is probably caused by a difference in the chemical interactions between the radionuclides and the grouts.

The radionuclide, as well as the type of waste matrix, is important to evaluating a grout for use as a stabilization material. Compressive strength, porosity, and hydraulic conductivity are important parameters to consider when evaluating the immobilization potential of a grout for a specific contaminant, but none of them are a direct indicator of leach resistance. The addition of waste materials generally decreased the compressive strength and increased the hydraulic conductivity and porosity of the grouts compared to neat grout samples. These measurements suggest that the ability of grouts to immobilize contaminants decreased with the presence of waste. Based on results of ANS leach tests conducted on grouted samples alone, there is no clear best choice among formulations of grouts tested for all types of waste and contaminants. Based on current testing and past studies, the strongest performing grouts, considering physical properties, leaching, and cost, for each class of contaminant and waste are as follows:

- For TRU contaminants in soil, four grouts were evaluated: WAXFIX, GMENT-12, U.S. Grout, and TECT HG. In areas where physical support and immobilization of contaminants is needed, GMENT-12 would be preferred, as it performed the best overall.

- For TRU contaminants in organic sludge, four grouts were evaluated: WAXFIX, GMENT-12, U.S. Grout, and TECT HG. In this case, all of the grouts performed equally well at reducing leachability of TRU contaminants, but GMENT-12 had the highest compressive strength. If organic sludge is to be grouted and if compressive strength is important, then GMENT-12 would be the best choice.

- For TRU contaminants in nitrate salt, five grouts were evaluated: WAXFIX, GMENT-12, U.S. Grout, TECT HG, and Saltstone. In areas where carbon steel drums or nonmetal containers were used to contain TRU contaminants in nitrate salt, the integrity of the containers is likely already compromised, and jet grouting could be used to reduce the potential for contaminant transport. Where ISG has been identified for use in nitrate salts, U.S. Grout is recommended because it produces samples with the highest compressive strength and a comparable leach index to the other grouts tested. WAXFIX also produced good leach-resistant samples and could withstand high salt loadings; however, the compressive strength was not as good as U.S. Grout.

- For non-TRU contaminants in soil, ten grout formulations were evaluated: WAXFIX, GMENT-12, U.S. Grout, TECT HG, Saltstone, Portland cement, Portland cement with fly ash, Portland cement with slag, Portland cement with fly ash and thiosulfate, and Portland cement with slag and thiosulfate. Portland cement with slag, Portland cement with slag and thiosulfate, WAXFIX, and GMENT-12 would be the best and essentially equal choices for immobilization of C-14, Tc-99, and I-129 in soil. Based on physical properties, GMENT-12 compared to Portland cement with slag has the same compressive strength and porosity and lower hydraulic conductivity. WAXFIX compared to GMENT-12 and Portland cement with slag has lower compressive strength, lower porosity, and equal hydraulic conductivity. If cost is considered, then Portland cement with slag will be the best choice.

- WAXFIX is recommended for ESG of nitrate salt waste. Most Portland cement-based grouts do not tolerate high loadings of salts. Based on the test results, Saltstone, a Portland cement-based grout, might work effectively with some modification to the recipe used in this report. WAXFIX, a paraffin based grout, was able to tolerate high concentrations of salts and maintain a cohesive sample.

- If ISG were used for physical support of a cap, then a cementitious grout would be the preferred choice. Overall, Portland cement with slag, GMENT-12, or U.S. Grout would be the best choices for physical support of the cap. Based on unconfined compressive-strength tests, GMENT-12 was the most tolerant of organic sludge, U.S. Grout was the most tolerant of nitrate salt, and soil was tolerated equally by all three. Since nonproprietary grouts, such as Portland cement with slag, are expected to be less expensive than proprietary grouts, and since volume percentage of organic sludge and nitrate salt waste in the SDA is relatively small, Portland cement with slag is recommended for use as a cap support grout in the SDA.

ACKNOWLEDGEMENTS

This report embodies the cooperative effort of numerous technical and support staff, without whose many contributions and commitment to excellence this work would not have been possible. The authors would like to recognize and express their gratitude to John Dick, Rick Demmer, Bruce Mincher, Robert Kirkham, Kristine Baker, Alan Herbst, Steve Johnson, and Marvin Banks who performed experimental work, drafted appendixes, and contributed to sections of this report.

CONTENTS

FIGURES

TABLES

ACRONYMS

ANS	American Nuclear Society
COC	contaminant of concern
DSC	differential scanning calorimetry
EDTA	ethylenediaminetetraacetic acid
ESG	ex situ grouting
ICP-MS	inductively coupled plasma-mass spectrometry
INL	Idaho National Laboratory
ISG	in situ grouting
ISTD	in situ thermal desorption
K_d	partition coefficient
OU	operable unit
PNNL	Pacific Northwest National Laboratory
RFP	Rocky Flats Plant
RI/FS	remedial investigation and feasibility study
RWMC	Radioactive Waste Management Complex
SDA	Subsurface Disposal Area
TGA	thermal gravimetric analysis
TRU	transuranic
VOC	volatile organic compound
WAG	waste area group

Preremedial Design Report of Remediation Options for OU 7-13/14

1. INTRODUCTION

This report presents results of testing based on the *Test Plan for the Evaluation of In Situ Thermal Desorption and Grouting Technologies for Operable Unit 7-13/14* (Yancey et al. 2003) and makes recommendations for consideration during development of the feasibility study for Operable Unit 7-13/14. Grouting treatment options are being considered for radioactive waste buried in the Subsurface Disposal Area (SDA), a radioactive landfill that is part of the Radioactive Waste Management Complex (RWMC) at the Idaho National Laboratory (INL) Site (see Figure 1). The grouting treatment options include in situ grouting (ISG) and ex situ grouting (ESG). In addition to grouting, in situ thermal desorption (ISTD) was evaluated.

When the test plan (Yancey et al. 2003) was prepared, the three treatment options (ISTD, ISG, and ESG) included in it were being evaluated and were all under consideration for use in developing remedial alternatives for the feasibility study. Since the test plan was written, data gathered through the test plan evaluations, the *Second Addendum to the Work Plan for the OU 7-13/14 Waste Area Group 7 Comprehensive Remedial Investigation/Feasibility Study* (Holdren and Broomfield 2004), and the *Feasibility Study Preliminary Documented Safety Analysis for In Situ Thermal Desorption in the Subsurface Disposal Area* (Abbott 2003) have led to the elimination of ISTD as a treatment option for the feasibility study. The results, conclusions, and recommendations from ISTD testing are included in this report to document the testing conducted as a part of the test plan by Yancey et al. (2003).

In situ grouting and ESG can physically stabilize waste and slow the release and migration of most hazardous inorganics and radionuclides. In addition, ISG-treated areas of the SDA can minimize subsidence and support a future surface barrier to reduce water infiltration into the waste. In situ thermal desorption focuses on removal of organics but also can remediate nitrate salts and chlorinated organics in organic sludge.

Grouts under consideration for ISG—neat and with various admixtures—were tested for (1) durability, (2) characteristics that tend toward leaching or binding of contaminants, and (3) data to support contaminant transport modeling for treated waste forms. For ISTD testing, major emissions, quantified as waste and soil, were slowly heated to determine the degree of hazardous organic contaminant and nitrate removal, or destruction from test samples. Potential mixtures of organics and nitrates were tested for reactivity. These tests were guided by the test plan by Yancey et al. (2003).

1.1 Purpose

This report provides additional data for the U.S. Department of Energy to aid in determining the effectiveness of ISG and ESG as treatments for waste at the SDA. Some of the data generated during these tests will support the remedial investigation and feasibility study (RI/FS) for Waste Area Group (WAG) 7 Operable Unit (OU) 13/14.[a] The SDA is being remediated under the Comprehensive Environmental Response, Compensation, and Liability Act (42 USC § 9601 et seq., 1980). The tests reported in this document address Comprehensive Environmental Response, Compensation, and Liability

a. The *Federal Facility Agreement and Consent Order* (DOE-ID 1991) lists 10 WAGs for INL. Each WAG is subdivided into OUs. The RWMC is identified as WAG 7 and originally contained 14 OUs. Operable Unit 7-13 (TRU pits and trenches RI/FS) and OU 7-14 (WAG 7 comprehensive RI/FS) ultimately were combined into the OU 7-13/14 comprehensive RI/FS for WAG 7.

Act criteria of effectiveness, both near and long term; reduction in mobility of contaminants through stabilization; and implementability. This document follows the organization and processes identified in guidance from the U.S. Environmental Protection Agency (EPA 1992).

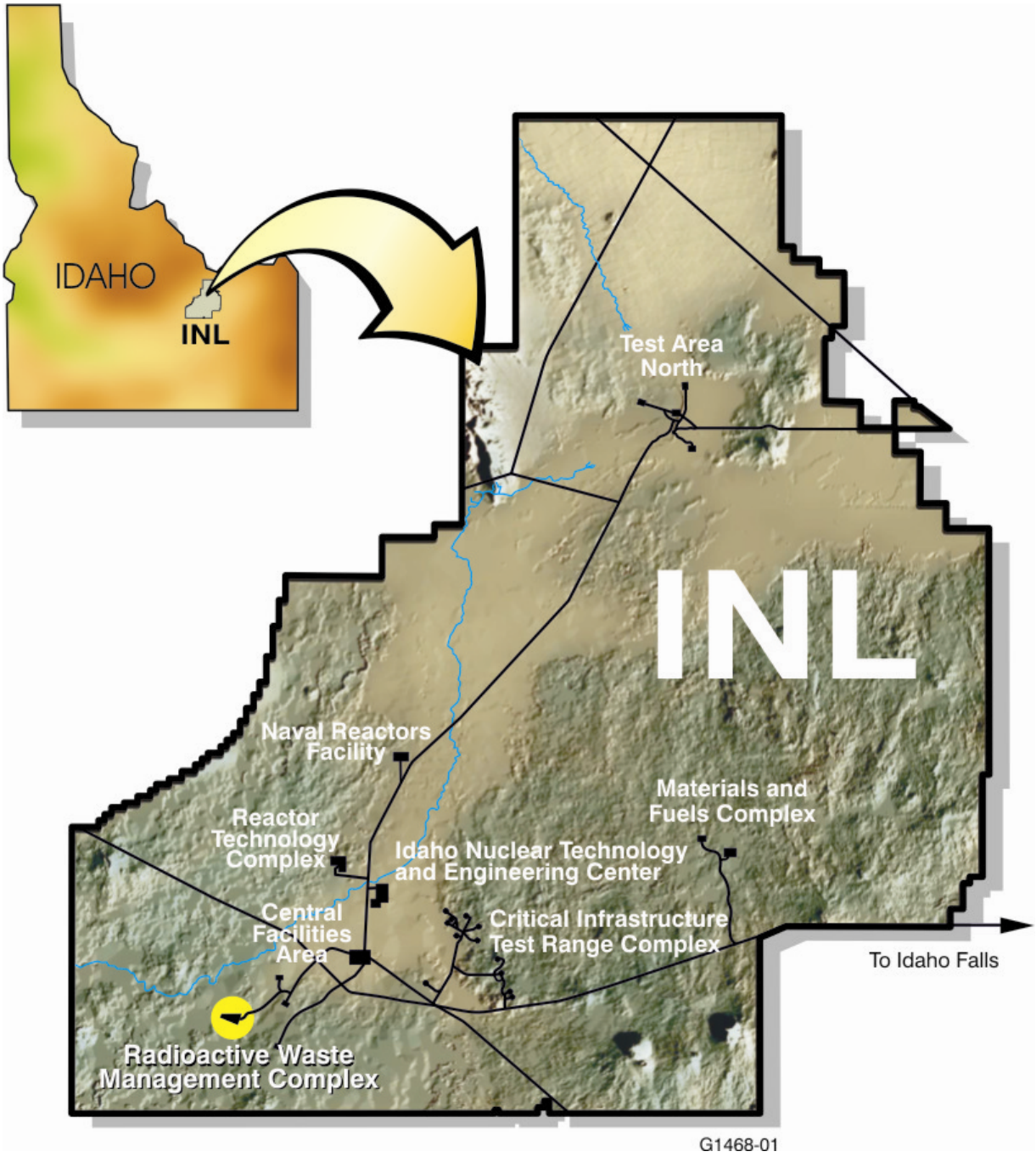

Figure 1. Map showing Radioactive Waste Management Complex and other major facilities.

1.2 Scope

The tests reported in this document focus on thermal treatment and stabilization of radioactive mixed waste buried in the SDA and follow Yancey et al. (2003). Twenty tests are described, and the results are reported in this document.[a] Based on results of the originally planned tests, four tests (hydraulic conductivity, porosity, compressive strength, and leaching) were repeated with four additional grout formulations. Tests for ISTD and ISG used transuranic (TRU) waste from the SDA and surrogate. The ISG tests also used surrogate non-TRU waste. The ESG bench tests used waste from Pad A.

A series of cold (nonradioactive) tests established the approach for hot (radioactive) testing. Hot tests used surrogates spiked with radionuclides (isotopes of uranium, plutonium, americium, neptunium, iodine, carbon, and technetium were used, as appropriate, for specific tests), waste material retrieved from Pit 9 by the OU 7-10 Glovebox Excavator Method Project (DOE-ID 2004), and material from Pad A. All preparations for hot testing, including safety documentation, were completed before accepting material from Pit 9 or Pad A and are documented separately.

The screening process in Zitnik et al. (2002) streamlined the list of available remedial technologies and process options, retaining for subsequent development and screening only those that met the criteria adequately. The effectiveness of these remaining technologies is presented in this report through results of bench and laboratory tests.

1.3 Site Description

The Idaho National Laboratory Site is located in southeastern Idaho and occupies 2,305 km^2 (890 mi^2) in the northeastern region of the Snake River Plain. Regionally, the INL Site is nearest to the cities of Idaho Falls and Pocatello and to U.S. Interstate Highways I-15 and I-86. The INL Site extends nearly 63 km (39 mi) from north to south, is about 58 km (36 mi) wide in its broadest southern portion, and occupies parts of five southeast Idaho counties. Public highways (i.e., U.S. 20 and 26 and Idaho 22, 28, and 33) within the INL Site boundary and the Experimental Breeder Reactor I, which is a national historic landmark, are accessible without restriction. Otherwise, access to INL Site is controlled. Neighboring lands are used primarily for farming or grazing, or are in the public domain (e.g., national forests and state-owned land) (Zitnik et al. 2002).

The SDA landfill, established in 1952, was originally called the National Reactor Testing Station Burial Ground. The original landfill covered 5.2 ha (13 acres) and was used for shallow land disposal of solid radioactive waste. In 1958, the SDA was expanded to 36 ha (88 acres). Relocating the security fence in 1988 outside the dike surrounding the SDA established its current size of 39 ha (97 acres). The Transuranic Storage Area was added to the RWMC in 1970. Located next to the east side of the SDA, the Transuranic Storage Area's 23 ha (58 acres) is used to store, prepare, and ship retrievable TRU waste to the Waste Isolation Pilot Plant, southeast of Carlsbad, New Mexico. The 9-ha (22-acre) administration and operations area at the RWMC includes administrative offices, maintenance buildings, equipment storage, and miscellaneous support facilities (Holdren et al. 2002). See Figure 2 for a map of the physical layout of all RWMC disposal locations and facilities.

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b. After the test plan was completed, four tests—macroencapsulation, microencapsulation, plutonium aerosolization, and fracture propagation—were delayed until results of tests recorded in this report were available. These four tests originally were described in the test plan but had not been conducted at the time this report was written.

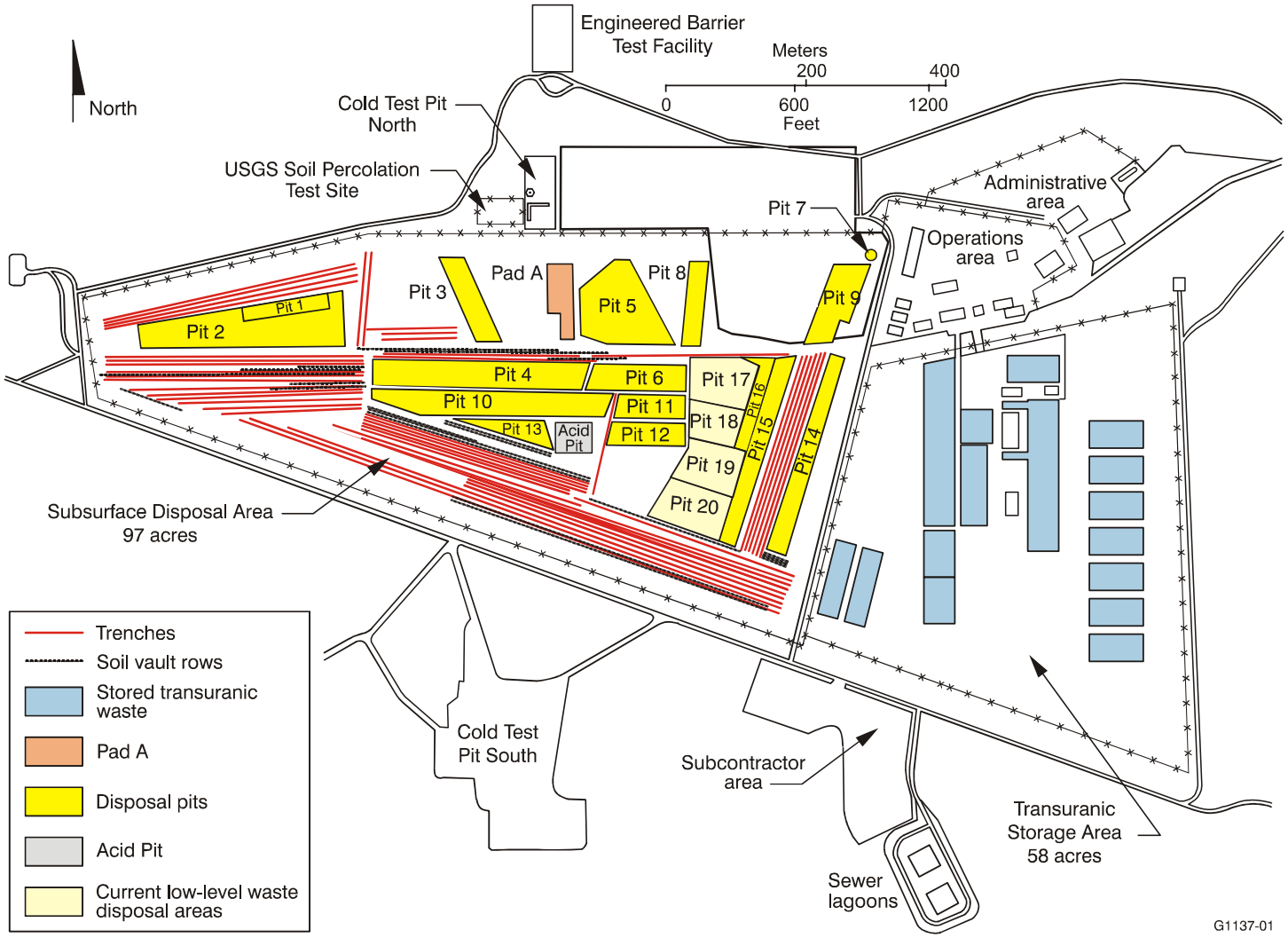

Figure 2. Map of the Radioactive Waste Management Complex showing the location of the Subsurface Disposal Area and types of buried waste.

1.3.1 Brief History of Site Operations

Disposal of mixed waste containing hazardous chemical and radioactive contaminants was allowed through 1984. Since 1985, waste disposals in the SDA have been limited to low-level radioactive waste generated at the INL Site. Construction, operation, and decommissioning of INL programs for nuclear reactor testing have resulted in large volumes of waste. Various containers were used in shipping and disposing of waste, including steel drums, cardboard cartons, and wooden boxes. Larger, individual items—such as tanks, furniture, process and laboratory equipment, engines, and vehicles—were placed separately as loose trash (Zitnik et al. 2002).

Contaminants—disposed of in shallow subsurface disposal units consisting of pits, trenches, and soil vaults—include hazardous chemicals, remote-handled fission and activation products, and TRU radionuclides. Disposals of TRU and mixed waste—mostly from Rocky Flats Plant (RFP) in Colorado—were allowed through 1970. Radioactive waste from offsite sources originated from a variety of facilities, including military and other defense agencies, universities, commercial operations, and the Atomic Energy Commission (Zitnik et al. 2002).

1.4 Description of Buried Waste

Several waste types at the SDA include the nitrate salts in Pad A and combustibles, soil, and three types of sludge (inorganic, organic, and nitrate salt) in TRU and non-TRU pits and trenches. Based on recent mapping and burial records, nitrate or organic sludge drums are found in 20% or less of four pits (Becker et al. 1998; Salomon et al. 2003). The density of organic sludge drums is usually less than 4.5 drums/m^2; the density of nitrate salt drums is less than 1.6 drums/m^2. High-density areas greater than this occur in less than 10% of the total drum area. Thus, areas of high density are rare.

The results presented in this report are from tests conducted with surrogates and wastes. The surrogates were prepared based on the expected composition of the waste and with and without radionuclides (hot and cold surrogates, respectively). The wastes were[d] samples retrieved from locations within the SDA, that is organic sludge waste was retrieved from Pit 9 and Pad A waste was retrieved from Pad A. The primary TRU contaminants of concern (COCs) that were used in this study are americium, plutonium, uranium, and neptunium. The non-TRU COCs include technetium, iodine, and C-14 (Holdren et al. 2002).

1.4.1 Organic Sludge Waste and Surrogate

Organic sludge from Pit 9 contains chlorinated volatile organic COCs, such as trichloroethene, trichloroethane, tetrachloroethene, methylene chloride, and carbon tetrachloride, in addition to the TRU COCs (Holdren et al. 2002). Two different estimates of organic sludge waste compositions have been developed based on several reports: Clements (1982), Vigil (1990), Liekhaus (1991), and Arrenholz and Knight (1991). The earlier 1982 and 1989 assessments gave the approximate organic liquid content of SDA sludge based on sludge preparation and shipping records. The 1991 assessments have been updated based on the following:

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[d] Samples were taken during operation of the OU 7-10 Glovebox Excavator Method Project, which retrieved 59 m^3 (77 yd^3) of buried waste from the SDA during December 2003 and January 2004 (DOE-ID 2004). The purpose of the Glovebox Excavator Method Project was to demonstrate the feasibility of waste retrieval, provide information on any COCs present in the underburden, and characterize waste-zone material for safe and compliant storage pending a decision on final disposition. The Glovebox Excavator Method Project operated under the *Federal Facility Agreement and Consent Order for the Idaho National Engineering Laboratory* (DOE-ID 1991) and the "Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA/Superfund)" (42 USC § 9601 et seq., 1980).

- Calculations from recent vapor removal by the Organic Contamination in the Vadose Zone system
- Newly found records as RFP sludge preparation areas are decontaminated
- Recent shallow sampling of organic vapor between waste pits.

The current composition is now hypothesized to be 21 to 27 vol% Texaco Regal Oil,[e] 11 to 23 vol% miscellaneous oil, 20 to 37 vol% carbon tetrachloride, and 30 vol% other chlorinated hydrocarbons (details of the composition are presented in Appendix A).

The primary halogenated hydrocarbon COC in the organic sludge is carbon tetrachloride. Calcium silicate, Oil Dri, Microcel E, or other sorbent material was added as an absorbent for organic liquids (Texaco Regal Oil) (Miller and Varvel 2005). The Texaco Regal Oil used at RFP is no longer manufactured.

1.4.2 Pad A Waste and Nitrate Salt Sludge

Composition of Pad A waste includes salt at 30 wt% potassium nitrate and 60 wt% sodium nitrate flakes with about 400 ppm soluble chromate (such as Cr^{+6}) and 180 pCi/g uranium as the primary hazardous and radioactive components (a detailed composition is provided in Appendix A). While nitrate and total chromium are issues with the nitrate salt sludge, the only contaminant of concern is uranium. The primary components of nitrate salt sludge (RFP Series 745 sludge) are sodium nitrate and potassium nitrate in an approximate 2-1 ratio. The composition of the Pad A waste and the nitrate salt sludge waste are essentially the same. Since nitrate salt sludge waste was not retrieved from Pit 9, Pad A waste was used for testing. Nitrate salt sludge surrogate (without radionuclides) was also prepared for testing as required. The nitrate salt sludge COCs are nitrates and uranium (Holdren et al. 2002).

1.4.3 Inorganic Sludge Surrogate

The inorganic sludge surrogate formulation is based on average composition of inorganic precipitates in original RFP Series 741 and 742 sludge (Landman 1981; Clements 1982) and previous surrogates developed to represent this sludge (Low 1985; Low et al. 1987; Loomis and Low 1988) as shown in Appendix A. The inorganic sludge surrogate will contain RWMC lake-bed soil, other inorganic salt, water with terbium added, and nitrate salt. The RFP waste is estimated to have contained 40 to 70 wt% water, to which 10 to 20 wt% cement was added when the sludge was placed in drums. At 20 wt% cement, the sludge-cement mixture would likely resemble a consolidated rather than an unconsolidated material. To be conservative with respect to evaluating the performance of ISG and ISTD, the amount of water and cement has been minimized to maximize the concentration of inorganic salts and create an unconsolidated material. This approach is consistent with previous testing activities (Low 1985; Low et al. 1987; Loomis and Low 1988).

1.5 Document Organization

The following paragraphs briefly describe the remaining sections in this report:

- Section 2 describes treatment technologies under consideration
- Section 3 introduces testing

e. References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise do not necessarily constitute or imply endorsement, recommendation, or favoring by the U.S. Government, any agency thereof, or any company affiliated with the Idaho Cleanup Project at the Idaho National Laboratory Site.

- Section 4 discusses each test series for ISTD and integrates the results
- Section 5 discusses each test series for ISG and integrates the results
- Section 6 discusses each test series for ESG and integrates the results
- Section 7 contains conclusions and recommendations
- Section 8 lists the references cited throughout this report
- Appendix A contains the recipes used in the tests and details of compositions mentioned in the body of the report
- Appendixes B through T describe the study approach and test design and contain the results for each test series.

2. DESCRIPTION OF TREATMENT TECHNOLOGIES

The following sections describe the three treatment technologies—ISTD, ISG, and ESG—for which evaluation data were collected during this study.

2.1 In Situ Thermal Desorption

In situ thermal desorption is commercially available and has been applied successfully at sites containing soil contaminated with organics (TerraTherm 2005a; Vinegar et al. 1998; Vinegar, Stegemeier, and Sheldon 1997); however, ISTD has not been demonstrated at sites containing buried containerized waste, radionuclides, nitrate salts, reactive mixtures, or large amounts of metal debris. In situ thermal desorption was being considered for areas in the SDA with high concentrations of volatile organic compounds (VOCs). The ISTD process considered using electric resistance heaters to heat a region of the subsurface soil and waste (see Figure 3) to a prescribed temperature. Vapors generated by this heating process are collected and treated by an aboveground off-gas system. In situ thermal desorption can reduce the amount of contaminants in the subsurface by volatilization or, at higher temperatures, by degradation. Results from bench- and drum-scale tests presented later in this report have shown that there are conditions where potential to have uncontrolled reactions exists. Other evaluations (Abbott 2003) have identified the potential consequences of uncontrolled reactions. Because of these findings, ISTD is not recommended as a stand-alone treatment or a pretreatment for ISG at the SDA. The discussion that follows describes the ISTD system and presents the results of the evaluations performed.

In most applications of ISTD, two types of boreholes are used. One type provides heat and vapor removal; it contains an electrical resistance heater within a sealed metal pipe. The metal pipe sits within a perforated metal casing. Vapor is removed through the annulus between the two pipes. The second type of borehole provides heat only; it also contains an electrical resistance heater in a sealed pipe, which is also closed at the surface. The boreholes are spaced 2.1 to 3 m (7 to 10 ft) apart (U.S. Navy 1998) for removal of higher boiling-point compounds and 3 to 6.1 m (10 to 20 ft) apart for lower boiling-point compounds (TerraTherm 2005a). Heat is transferred to surrounding media by conduction. Heating boreholes are placed around heating-and-vapor-removal boreholes (see Figure 3). Heaters in boreholes can operate at temperatures of up to 1,000°C (1,832°F) (U.S. Navy 1998; Abbott 2003), although generally they operate at 400 to 800°C (752 to 1,472°F) (TerraTherm 2005a; Yancey et al. 2003).

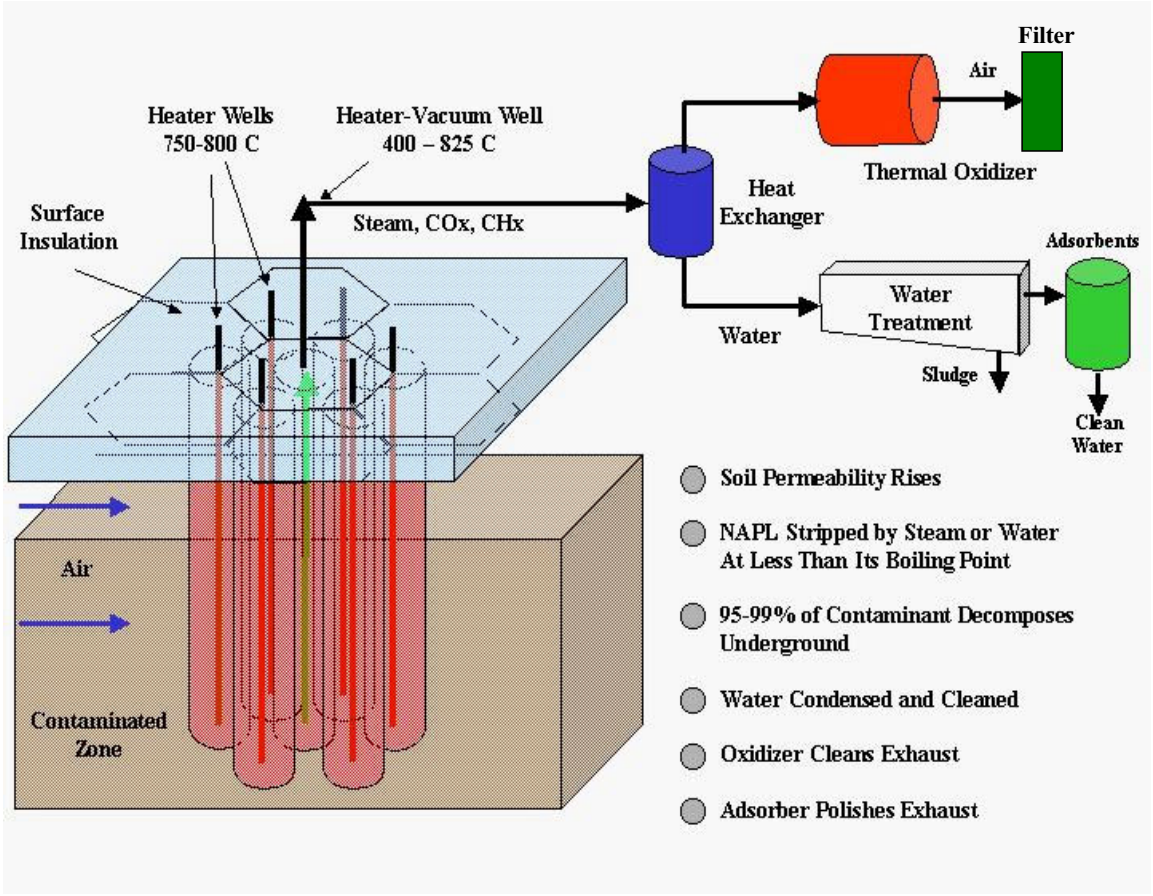

Figure 3. Schematic of ISTD process.

The ISTD process can effectively destroy nitrate salt as a potential oxidizer at temperatures above 310°C (590°F). Reactivity studies have been done on surrogate and waste salt. Heating past the eutectic melting point of salt (210 to 250°C [410 to 482°F]) to decomposition (270 to 310°C [518 to 590°F]) effectively destroys sodium nitrate and potassium nitrate, which are potential oxidizers. However, if sufficient nitrates are present in intimate contact with finely divided reducing material such as carbon, reactions may be induced before decomposition is complete.

In situ thermal desorption can be done at a range of treatment-zone temperatures (TerraTherm 2005a). Lower treatment-zone temperatures (100 to 200°C [212 to 392°F]) are appropriate for removing VOCs and water; this is the temperature range of interest for the SDA. Higher treatment-zone temperatures (greater than 200°C [392°F]) are used for removing and destroying semivolatile compounds. Treatment-zone temperatures of 400 to 500°C (752 to 932°F) have been used to remove and destroy polychlorinated biphenyls at some field sites (TerraTherm 2005b; TerraTherm 2005c; U.S. Navy 1997). Spacing of boreholes and operating temperature of heaters depend on the nature of the contamination, the rate of removal desired, the physical properties of soil or waste to be treated, and the compounds targeted for treatment.

The ISTD system was designed for organic contaminated soil but can be used on buried debris. During the ISTD process, buried waste is heated to cause chemical and physical changes both in the matrix and the contaminants. Organics are volatilized or decompose. Nonvolatile metals and radionuclides may remain unchanged or partition into new or altered phases of soil and waste during

treatment. Though the primary purpose of ISTD is to destroy organic contaminants, any retardation of actinide leaching is desirable.

In this study, ISTD has been evaluated at four temperatures: 20, 105, 275, and 450°C (68, 221, 527, and 842°F). At low temperatures, this technique has the potential to remove significant quantities of volatile and semivolatile organics. At higher temperatures, this technique has potential to degrade nitrate salt and some organic compounds and possibly remove them completely. The testing focused on criteria specific to the SDA application, such as release of acid gases, interaction of nitrate salts and organics, and fixation of actinides on soil or waste, as a result of heating to demonstrate effectiveness.

2.2 In Situ Grouting

In situ grouting is being considered for treatment of TRU pits and trenches, ISTD pretreated TRU pits and trenches, and non-TRU pits and trenches and soil vault rows. Jet grouting is the specific ISG technique being considered for buried waste within the SDA. Jet grouting uses a specially designed rotary-percussion drill rig to deliver and intimately mix grout with soil, debris, and contaminants in the subsurface (see Figure 4). For purposes of this report, ISG will refer to jet grouting. The grout is injected at approximately 6,000 psi through small nozzles; the high pressure, combined with the dense grout, provides the energy required to mix the grout and subsurface materials.

Information gathered in previous testing (Loomis et al. 2003) indicates that the jet-grouting process will not always cut through a waste drum.[f] The jet-grouting process, therefore, is accomplished on a 51-cm (20-in.) triangular pitch matrix, which guarantees that each 55-gal drum will be punctured and filled with as much grout as the voids in the drum will allow (see Figure 5). In addition, with that matrix, each large box will be punctured with multiple applications of grout. Each injection of grout in homogenous soil forms a column, and a series of diagonally offset and connected columns forms a monolith (Loomis et al. 2003). Testing in the field has shown these jet-grouted monoliths to be regions with intimately mixed grout and waste, the spacing of jet-grouting processes resulting in overlapping columns that do not maintain distinct boundaries. The monolith is not homogenous (unless the waste is homogenous in the region the monolith is placed); it is a series of contiguous mixed regions. Overlapping column placement decreases potential for voids in the final monolith and results in a unified mass from a set of discrete injection points. The degree of overlap among columns depends on the injection pressure, grout density, waste density, void space, container form, and debris content.

Grouts must be designed specifically for ISG to meet viscosity, particle size, and set times required for effective operation of the grouting rig. Past bench- and field-scale testing (Loomis et al. 2003) have demonstrated the implementability parameters (Shaw 2004) of the grout formulations being tested, specifically, GMENT-12, U.S. Grout, TECT HG, Saltstone, and WAXFIX. In addition, it is anticipated that the Portland-cement grouts tested will also be able to meet the implementability requirements (e.g., viscosity, particle size, and set times). GMENT-12, U.S. Grout, and TECT HG (proprietary Portland-cement-based formulations); nonproprietary Portland-cement-based formulations; and WAXFIX grout materials have been evaluated to determine the effectiveness of each grout based on leaching and physical characteristics to develop a recommendation for a single material for each application.

f. To cut through a waste drum, the nozzle must be very close to the drum, and the jet must be in contact with the drum long enough to erode or puncture the drum. Corroded metal is easier to cut through than noncorroded metal.

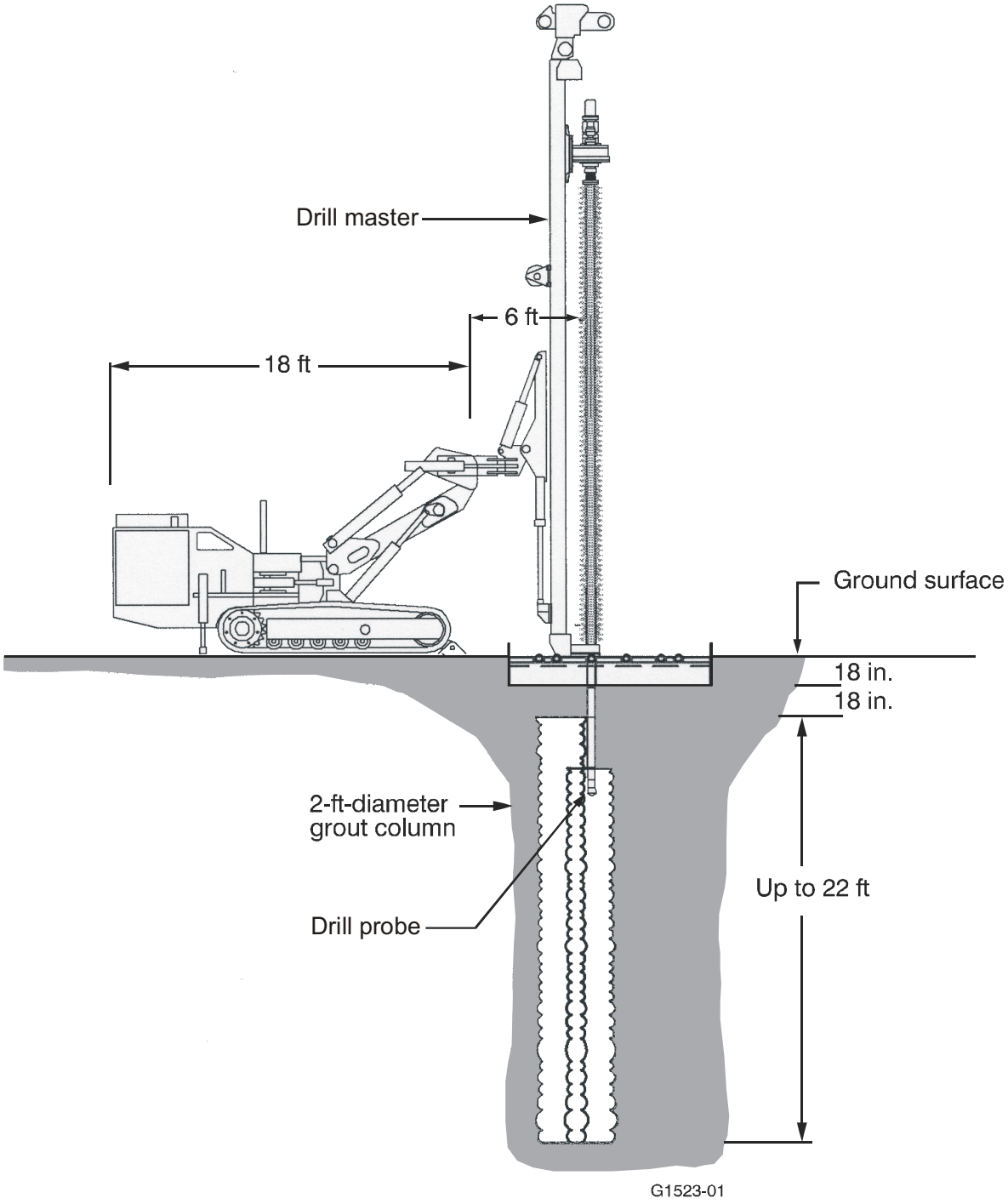

Figure 4. Preconceptual schematic of the overall process of in situ jet grouting.

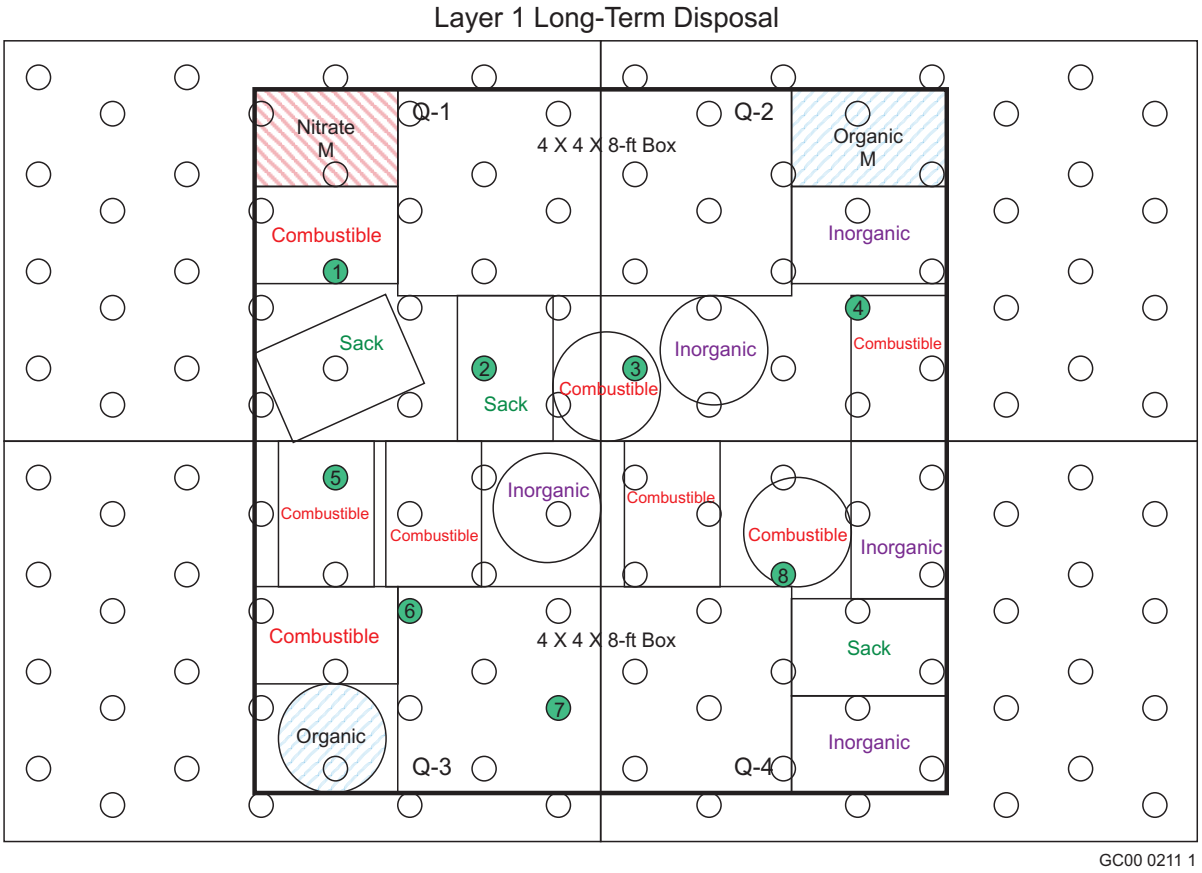

Figure 5. Example of 20-inch, triangular-pitch, jet-grouting pattern.

2.3 Ex Situ Grouting

Ex situ grouting (solidification) is being considered for treatment of the Pad A salt waste. Ex situ grouting includes selection of an appropriate grout and an approach to transfer the waste from Pad A to a mixing system where containers could be opened, waste contents mixed with grout, and grout-waste mixture placed in containers for disposal. Three candidate grouts[g] have been identified for testing: Polysiloxane, Saltstone, and WAXFIX.

3. TESTING

The tests in this report address six main objectives from Yancey et al. (2003):

1. **Develop data to support contaminant transport modeling for treated waste forms.** Data obtained from these tests will be used in modeling migration of contaminants in the final waste form after ISG or ESG. In addition, these data will be used to determine changes in leachability of actinides from the waste and surrounding soil following ISTD heating. These data will support modeling to estimate the release rate of contaminants from the treated waste and compare it to the predicted release rate from untreated waste. The test results also will support risk assessment, the risk model, and evaluation of residual risk for the proposed alternatives for the feasibility study for OU 7-13/14.

g. Dimethyl Polysiloxane, marketed by Technology Visions Group, uses a polymer encapsulation technology (Loomis, Miller, and Prewett 1997) shown to successfully encapsulate surrogate salt materials. Saltstone grout, developed by Savannah River Site, has been developed for salt encapsulation. WAXFIX also is considered in the in situ portion of Yancey et al. (2003).

2. **Evaluate durability of grouted waste.** Physical property data will be obtained to compare grouts and waste loadings. Long-term physical stability of the grouted waste forms will be estimated from these near-term tests.

3. **Evaluate WAXFIX for use as a grout.** The purpose of these tests is to understand better the advantages and limitations of WAXFIX as a grout for TRU and non-TRU waste. The data will be used to address potential criticality and reactivity concerns that may be encountered with specific types and concentrations of contaminants. The ability of WAXFIX to contain radionuclides and nitrates is evaluated. In addition, the generation rate of hydrogen gas for WAXFIX mixed with radionuclides will be assessed because of the radiolysis process.

4. **Quantify major emissions as waste and soil are slowly heated.** Determining primary off-gas constituents and concentrations as waste and soil are heated will help identify the off-gas processing requirements for full-scale test planning. The carbon monoxide and carbon dioxide releases determine the relative amounts of combustion and pyrolysis occurring. The gas proportion measurements also could assist in monitoring the type of waste being heated and any nitrate organic reactions. In addition, these data will support the generation of safety and design data for OU 7-13/14.

5. **Determine the degree of hazardous organic contaminant and nitrate removal or destruction from soil and waste.** Quantifying the removal or destruction of chlorinated VOCs and nitrate salt in the waste will help establish anticipated efficiency of ISTD-mediated removal or destruction of COCs in the TRU pits and trenches waste. The data also will be used to generate design data for the pending feasibility study for OU 7-13/14.

6. **Test potential mixtures of organics and nitrates for reactivity.** Determining whether mixtures of nitrate salt sludge and organic sludge will react exothermically during heating by ISTD will help establish temperature ranges to avoid such reactions.

Twenty different tests were performed to address these objectives. Details of the objectives, design, apparatus, procedures, and results for each test are provided in Appendixes B through T of this report. The objectives were developed to assist in evaluation of three technologies—ISTD, ISG, and ESG—being considered for use in remedial alternatives for the SDA. The objectives that are applicable to each technology are shown in Table 1.

4. DATA ANALYSIS AND INTERPRETATION—ISTD

The primary goal at the SDA for ISTD is removal or destruction of organics. The presence of organic contaminants in the SDA is a concern in and of themselves, but they also complicate the grouting process, so removal of organics is of primary concern. The second goal is that the ISTD process be maintained within the established process controls. The third goal is that the ISTD process not mobilize contaminants more than has already occurred.

The discussions that follow cover the four test plan objectives for ISTD:

- Develop data to support contaminant transport modeling for treated waste forms (Section 4.1)
- Quantify major emissions as waste and soil are slowly heated (Section 4.2)
- Determine the degree of hazardous organic contaminant and nitrate removal or destruction from soil and waste (Section 4.3)

- Test potential mixtures of organics and nitrates for reactivity (Section 4.4).

This testing includes retrieved waste and surrogates, depending on the type of testing conducted.

Table 1. Applicability of test objective to each technology.

Objectives	Technologies		
	In Situ Thermal Desorption	In Situ Grouting	Ex Situ Grouting
1. Develop data to support contaminant transport modeling for treated waste forms	X	X	X
2. Evaluate durability of grouted waste		X	X
3. Evaluate WAXFIX for use as a grout		X	
4. Quantify major emissions as waste and soil are slowly heated	X		
5. Determine the degree of hazardous organic contaminant and nitrate removal or destruction from soil and waste	X		
6. Test potential mixtures of organics and nitrates for reactivity	X		

4.1 Develop Data to Support Contaminant Transport Modeling for Treated Waste Forms

Treatment of surrogate and waste by ISTD does not result in formation of consolidated material (test monoliths) required for American Nuclear Society (ANS) leach testing. Another useful indicator of contaminant mobility is the partition coefficient (K_d). Partition coefficients can be measured on unconsolidated material, such as ISTD-treated material. Estimates of K_d for rare earths and radionuclides were measured for ISTD-treated waste and surrogates. Evaluating the leachability of contaminants using K_d data helps to answer the question of the effects of ISTD on leachability.

4.1.1 Partition Coefficients for ISTD-Treated Nonradioactive Surrogates

Three types of surrogates expected to contain high amounts of TRU contaminants (organic sludge surrogate, inorganic sludge surrogate, and soil) were leach tested. The recipes for surrogates are included in Appendix A. Soil used in testing was from the RWMC area (where waste and soil reside) of the INL Site; it was dry and was sieved for uniformity.

Each of the surrogates was spiked with one or several of four rare-earth elements to simulate radionuclides. Four rare-earth elements were used in testing: terbium, lanthanum, cerium, and neodymium.

4.1.1.1 *Leaching of Surrogate and Soil.*

After heating to simulate ISTD treatment, solid residue from the organic sludge surrogate, inorganic sludge surrogate, and soil was allowed to cool to room temperature. Samples of material, 1 to 10 g (0.04 to 0.35 oz) in mass, were weighed to the nearest milligram and placed in polypropylene bottles. Enough simulated groundwater was added to each bottle so that the liquid-to-solid ratio was 10 mL (0.34 oz) liquid volume to 1 g (0.04 oz) solid mass. Generally, a 10-g (0.35-oz) sample was added to 100 mL (3.38 oz) of simulated groundwater. This extractant is the same pH-8 groundwater simulant used for grout leach testing. This simulated groundwater is prepared in a 50-L (13.2-gal) batch in accordance with the recipe in Table A-1 of Appendix A.

The samples were maintained at room temperature and stirred or shaken for 24 hours to allow for equilibration between the sample and the solution. The K_d is calculated in Equation (1):

$$K_d = [M]_{solid}/[M]_{solution} \quad (1)$$

where:

$[M]_{solid}$ = amount of metal assigned per unit mass of soil in milligram per kilogram

$[M]_{solution}$ = dissolved concentration of metal in equilibrium with the solid in milligram per liter.

In dilute solutions, a plot of $[M]_{solution}$ as a function of $[M]_{solid}$ should be linear. A regression analysis is performed on the plot, and the slope equals K_d. A full K_d analysis was beyond the scope of this work; measurements were taken at a single solid concentration. The data presented in this report provide a first approximation of K_d for the rare earths tested. The units of measure are milliliters per gram.

4.1.1.2 *Soil.*

Measured lanthanum, cerium, and neodymium occurred naturally in the soil, while terbium was added as an oxide to the soil. The K_ds for lanthanum, cerium, and neodymium remained fairly constant as the temperature increased (see Figure 6), while the K_d for terbium appeared to increase as the temperature increased above 275°C (527°F); there was no statistical difference between the four rare earths at 610°C (1,130°F). The mean K_d was on the order of 1E+06 for most of the rare earths and temperatures; the 95% confidence intervals for most of these same data were the same order of magnitude as the mean (see Table K-3 in Appendix K for details). No statistically significant differences exist in the K_ds between ISTD-treated and untreated material or among the rare earths. The results here do not provide any evidence to suggest that thermally treating the surrogate will result in a change in leachability as determined from the K_ds. The general concern here is that thermally treating the waste may alter the state or phase of the contaminant, or it may change the leachability of the contaminant due to a change in the matrix. In this case, we did not look directly at changes in the contaminants' phase or chemical state. The K_d test more generally looked at changes in the leachability, more likely due to changes in the waste matrix.

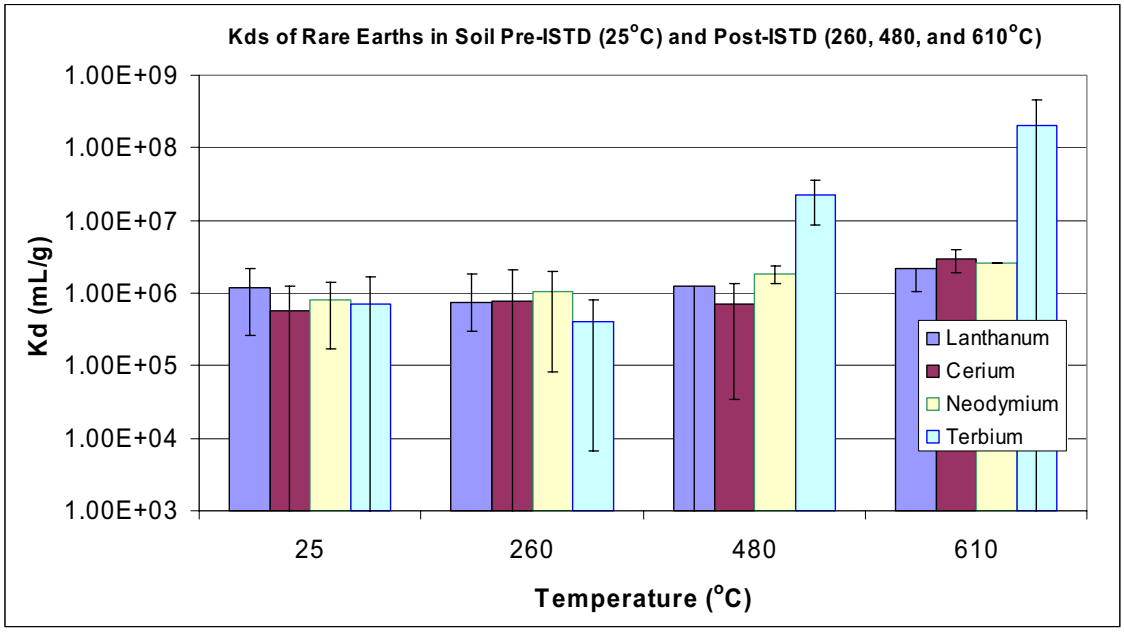

Figure 6. Partition coefficients of rare earths from soil.

4.1.1.3 Inorganic Sludge Surrogate. Lanthanum, cerium, and neodymium, as nitrates, and terbium, as an oxide, were added to the inorganic sludge surrogate. The K_ds for lanthanum, cerium, neodymium, and terbium remained fairly constant as the temperature increased (see Figure 7). The mean K_d was on the order of 1E+06 for most of the rare earths and temperatures; the 95% confidence intervals for these same data were the same order of magnitude as or one order larger than the mean (see Table K-4 in Appendix K for details). No statistically significant differences exist in the K_ds between ISTD-treated and untreated material or among the rare earths. Again, there is no evidence to suggest that thermally treating the waste will result in a decrease in the leachability or mobility of the contaminants tested.

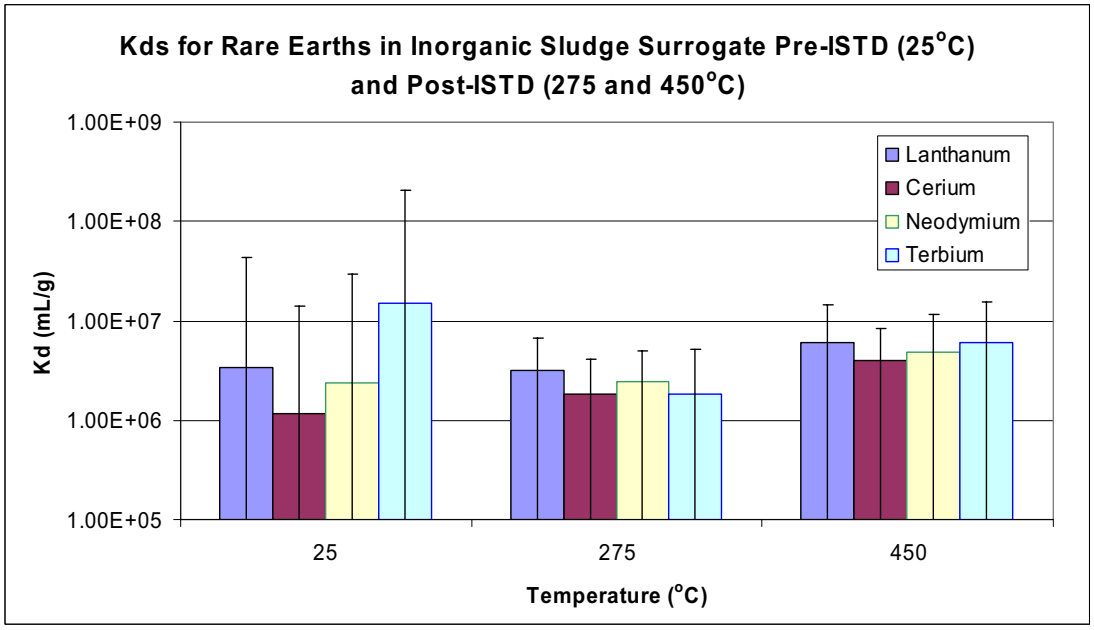

Figure 7. Partition coefficients for rare earths from inorganic sludge surrogate.

4.1.1.4 Organic Sludge Surrogate. Lanthium, cerium, and neodymium, as nitrates, and terbium, as an oxide, were added to the organic sludge surrogate. The K_ds for lanthanum, cerium, neodymium, and terbium appear to increase as the temperature increases (see Figure 8; error bars are not present for the 25 and 105°C (77 and 221°F) data because no replicates were taken for these points); however the 95% confidence interval for each of the rare earths at 650°C (1,202°F) exceeds the value of the mean. The mean K_ds spanned seven orders of magnitude: 1E+02 to 1E+09. The values of the 95% confidence intervals for these same data were the same order of magnitude or larger than the mean (see Table K-5 in Appendix K for details). Because of the high degree of variance, no statistically significant differences could be determined in the K_ds between ISTD-treated and untreated material, among rare earths or temperatures.

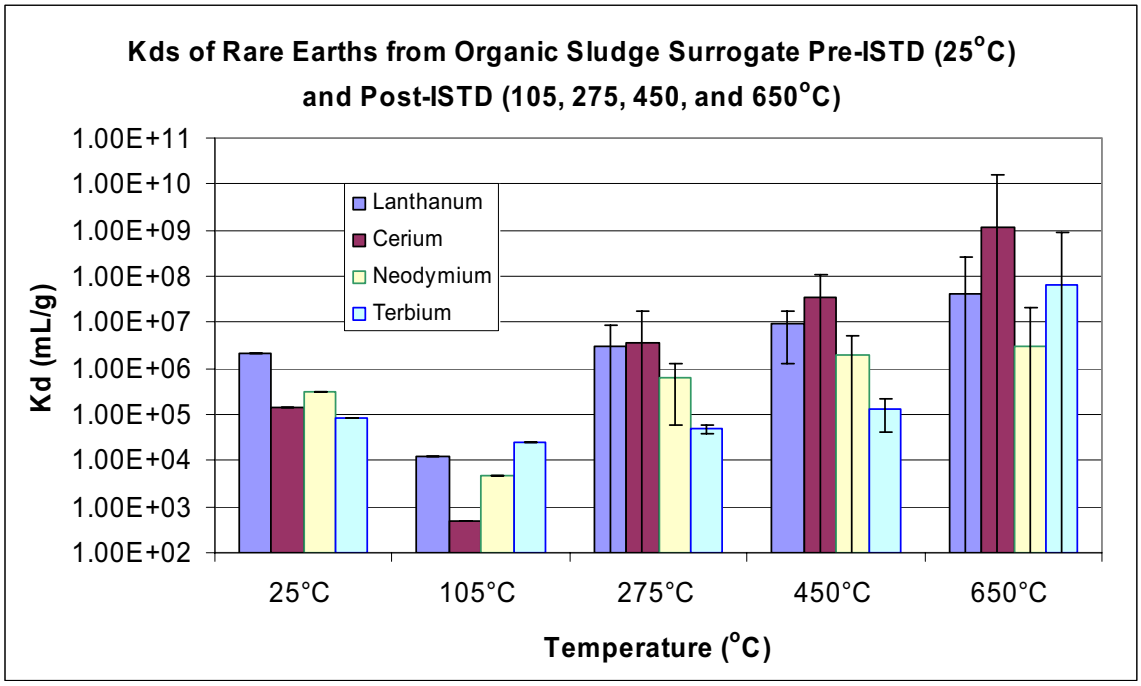

Figure 8. Partition coefficients for rare earths from organic sludge surrogate.

4.1.2 Partition Coefficients for ISTD-Treated Transuranic Surrogates and Waste

For soil from the INL Site spiked with radionuclides (americium, uranium, plutonium, and neptunium) and then processed by ISTD, the K_ds for americium, uranium, plutonium, and neptunium did not change significantly (compared to pre-ISTD) with temperature, except for neptunium at 450°C (842°F), where the K_d increased (see Figure 9). When radionuclides were tested, there was no benefit from the standpoint of decreasing leachability when the waste was thermally treated. The only exception is with americium, where there was an increased K_d for ISTD treatment at 450°C (842°F) compared to no ISTD. The results were statistically different at the 95% confidence interval.

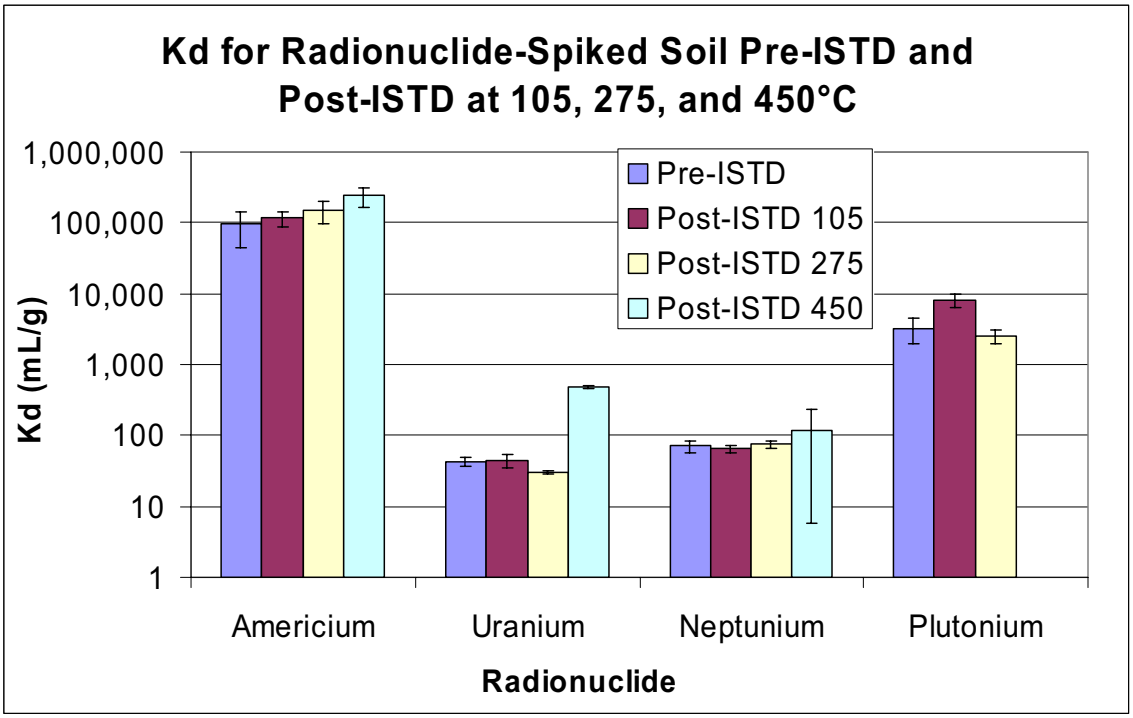

Figure 9. Partition coefficient for radionuclide-spiked soil pre-ISTD and post-ISTD at three temperatures.

For radionuclide-spiked inorganic sludge surrogate, the K_ds for americium and plutonium did not change with temperature (see Figure 10), suggesting that ISTD has no effect on the mobility of americium and plutonium. The K_ds for uranium were statistically higher (confidence interval) from pre-ISTD for 275 and 450°C (527 and 842°F), but there was no statistical significant difference between 275 and 450°C (527 and 842°F). This suggests that ISTD may reduce the mobility of uranium in inorganic sludge. The K_ds for neptunium at 275 and 450°C (527 and 842°F) were statistically lower (confidence interval) than for pre-ISTD, and the K_d at 450°C (842°F) was statistically lower than the K_d at 275°C (527°F). This suggests that ISTD may increase the mobility of neptunium in inorganic sludge. The reason for the difference in behavior among the four radionuclides is not known. Given the uncertainty in much of the data, only preliminary conclusions should be drawn from these results.

The K_d measurements shown in Figure 11 reveal that organic sludge surrogate partitioned similarly to the organic waste. Partition coefficients for uranium and plutonium were lower for the surrogate than for the waste pre-ISTD. Given the aging that could have occurred in the organic sludge waste, the uranium and plutonium in the surrogate could be more mobile than in the waste. Heating both the surrogate and waste sludge during ISTD treatment appears to have resulted in a less-leachable matrix, except possibly for americium; however, caution is advised in interpreting the results. The 95% confidence intervals were of the same magnitude as the mean for several data points. In addition, all metal concentrations in the aqueous phase were low. Small percent variances in these results near detection limit lead to large changes in K_d.

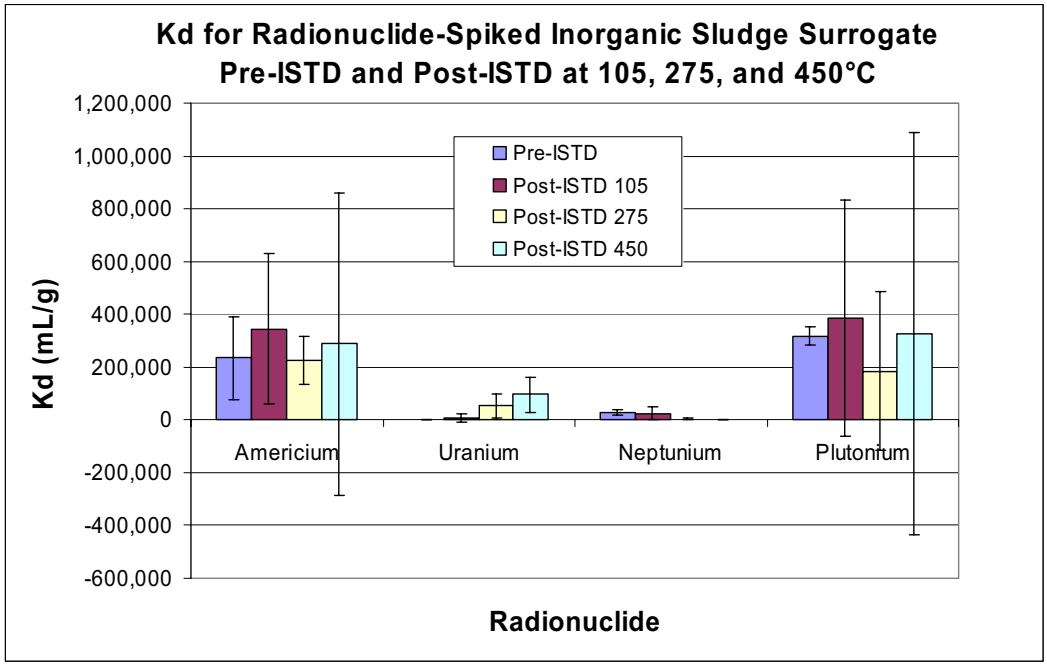

Figure 10. Partition coefficient for radionuclide-spiked inorganic sludge surrogate pre-ISTD (20°C [68°F]) and post-ISTD at three temperatures.

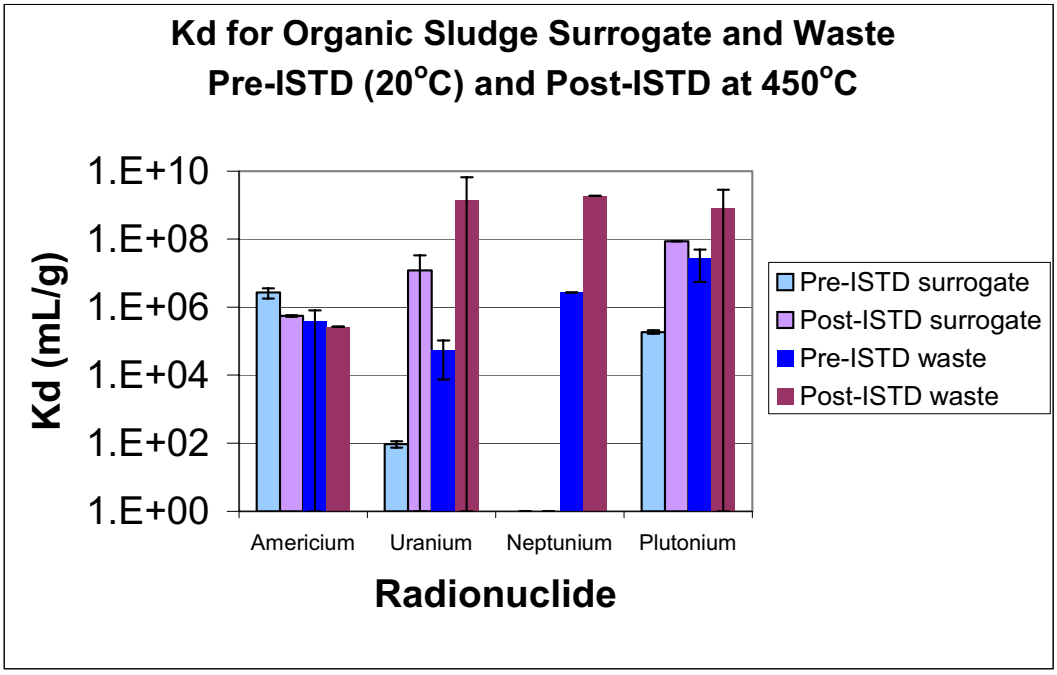

Figure 11. Partition coefficients for radionuclides in organic sludge surrogate (no neptunium added) and organic sludge waste pre-ISTD (20°C [68°F]) and post-ISTD (450°C [842°F]).

4.1.3 Conclusions for Contaminant Transport Modeling for ISTD

No clear pattern emerged from the K_d data for ISTD-treated surrogates and waste at the temperatures studied. In soil, only the K_d for neptunium showed an increase (significant at 95% confidence level) at an ISTD temperature of 450°C (842°F) compared to pre-ISTD. For inorganic sludge surrogate, the K_ds for uranium were higher (at 95% confidence level) than for pre-ISTD for 275 and 450°C (527 and 842°F), and the K_ds for neptunium at 275 and 450°C (527 and 842°F) were statistically lower (95% confidence level) than for pre-ISTD, meaning that the leachability of neptunium increased following ISTD treatment. For the organic sludge surrogate and waste, ISTD treatment appears to have resulted in a less-leachable matrix, except possibly for americium. Caution should be used in interpreting these results; all metal concentrations in the aqueous phase were low, and small percent variances in these results near detection limit lead to large changes in K_d.

One of the parameters tested for ISTD treated material was the ability of ISTD to reduce the leachability of the radionuclide COCs from the specific matrices. The results from this study do not provide evidence to show that this occurs. Only in the case of high-temperature ISTD of organic sludge does ISTD appear to provide a benefit by reducing leachability of radionuclides with the exception of americium. For soil from the INL Site and inorganic sludge, the leachability of the contaminant was usually unaffected as a result of the ISTD treatment, even at high temperatures.

4.2 Quantify Major Emissions as Waste and Soil are Slowly Heated

Surrogates (with and without radionuclides) and waste were used for tests in this section, as noted. The overall objective of this work was to better quantify the type of emissions that could be released during ISTD. Section 4.2.1 covers the work completed by MSE on nonradioactive surrogates. The MSE tests were larger drum-scale tests. Section 4.2.2 covers the ISTD of radioactive surrogate and waste completed at the INL Site, and was performed on a smaller scale using surrogate and waste that was ISTD treated. The second set of tests was used to confirm that the MSE drum-scale tests matched what would occur using the radioactive waste and surrogate.

4.2.1 MSE Drum Tests

The MSE vacuum thermal desorption system consists of a carbon-steel chamber sized to completely enclose a 55-gal test drum (see Appendix I for details of the equipment). For these tests, the system was operated under a slight vacuum (10.2 to 12.7 cm [4 to 5 in.] of water). The slight vacuum primarily was intended to simulate ISTD heating but also ensured that any gases released in the drum during thermal desorption were drawn into the off-gas treatment system, preventing leakage into the work area around the test bed.

To simulate airflow through soil into the slight vacuum of an ISTD heater assembly, air is metered by a mass flow control valve into the bottom of the 55-gal test drum where the air can be dispersed circumferentially around the drum by a distribution ring or injected at a point near the bottom of the drum. Six thermocouples monitored the temperature of the drum contents during heating: two near the center heater assembly, two halfway between the heater assembly and the drum wall, and two near the drum wall. The thermocouples are identified by position as top or bottom, and inner, middle, or outer.

A shakedown and four surrogate tests were conducted: organic sludge surrogate (Drum 1), nitrate salt surrogate (Drum 2), organic sludge surrogate with combustible debris surrogate (Drum 3), and organic sludge surrogate with combustible debris and soil (Drum 4). All of the tests were conducted with surrogate without radionuclides.

Because the temperature of the drum contents determined volatilization and pyrolysis of drum contents, the primary variable of interest for the ISTD drum tests was the temperature of the drum contents as a function of time. Temperatures of drum contents for the shakedown and the organic sludge, nitrate salt, and organic with combustibles tests are shown in Figure 12. Each line color in the graph indicates a particular test (e.g., green indicates the nitrate salt test [Drum 2]). The legend indicates the test and thermocouple locations as follows:

- The first two or three characters indicate the test: shakedown (Shk), organic sludge (Org), nitrate salt (Nit), organics with combustibles (D3), or organics with combustibles and soil (D4)
- The middle character indicates the thermocouple identifier
- The last two characters indicate the thermocouple locations, which were inner bottom (IB), inner top (IT), midbottom (MB), midtop (MT), outer bottom (OB), and outer top (OT).

As shown in Figure 12, heating rates and maximum temperatures varied substantially from test to test. Factors affecting heating rate were assumed to be power input to the heater, water content in the feed material, airflow into the drum, and fuel value of material volatilizing from the feed.

4.2.1.1 Shakedown Test. The objective of the shakedown test was to check out system components and to monitor the heating profile of the drum contents. The drum contents were a mixture of soil from the INL Site, kitty litter, Microcel E, and water, formulated to simulate the heat capacity, heat of vaporization, and total gas generation of the organic sludge. By using relatively inert constituents, a comparison of the shakedown test to the later organic sludge test (Drum 1) was expected to reveal any heating effects because of organic sludge chemical reactions. The details of the shakedown feed formulation are provided in Table I-2 of Appendix I.

The shakedown feed material was loaded into a 55-gal drum, which was then placed in the main test chamber of the barrel thermal desorption skid. For the shakedown test, electrical power was applied to the heater assembly for 65 hours. Nominal airflow into the test drum was 0.23 kg (0.5 lb)/minute.

4.2.1.2 Organic Sludge Surrogate Test (Drum 1). The organic sludge surrogate was a mixture of cutting oil, halogenated solvents, and adsorbents; a detailed recipe is provided in Table I-3 of Appendix I. All organic liquids in this surrogate have fuel value. Therefore, this mixture had the potential to react with injected air and produce heat. This combustion process, if it occurred, was expected to take place either within the heater assembly or in the hottest portion of feed material near the heater assembly. For the organic sludge test, electrical power was applied to the heater assembly for 22 hours. Nominal airflow into the test drum was 0.23 kg (0.5 lb)/minute.

Off-gas from the organic sludge test was sampled and analyzed for hydrogen chloride and chlorine gas (hydrochloric acid/chlorine) and the four VOCs included in the drum contents. As shown in Figure 13, the peak hydrochloric acid concentration, approximately 33 vol%, was reached 22 hours from the start of the test. Up to that time, there were no detectable feed VOCs in the off-gas. At 18 hours, when drum contents near the drum wall exceeded the target temperature of 105°C (221°F), the heater assembly was powered down. At 19 hours, combustion air to the drum was discontinued. Shortly after at 22 hours, the temperature of the drum contents began to decline, off-gas hydrochloric acid concentrations abruptly dropped off, and off-gas VOC concentrations abruptly increased. The VOC concentrations peaked at about 32 hours from the start of the test. At 35 hours, a nitrogen purge of the drum was started, which resulted in a dilution of the off-gas organics, as reflected in Figure 13.

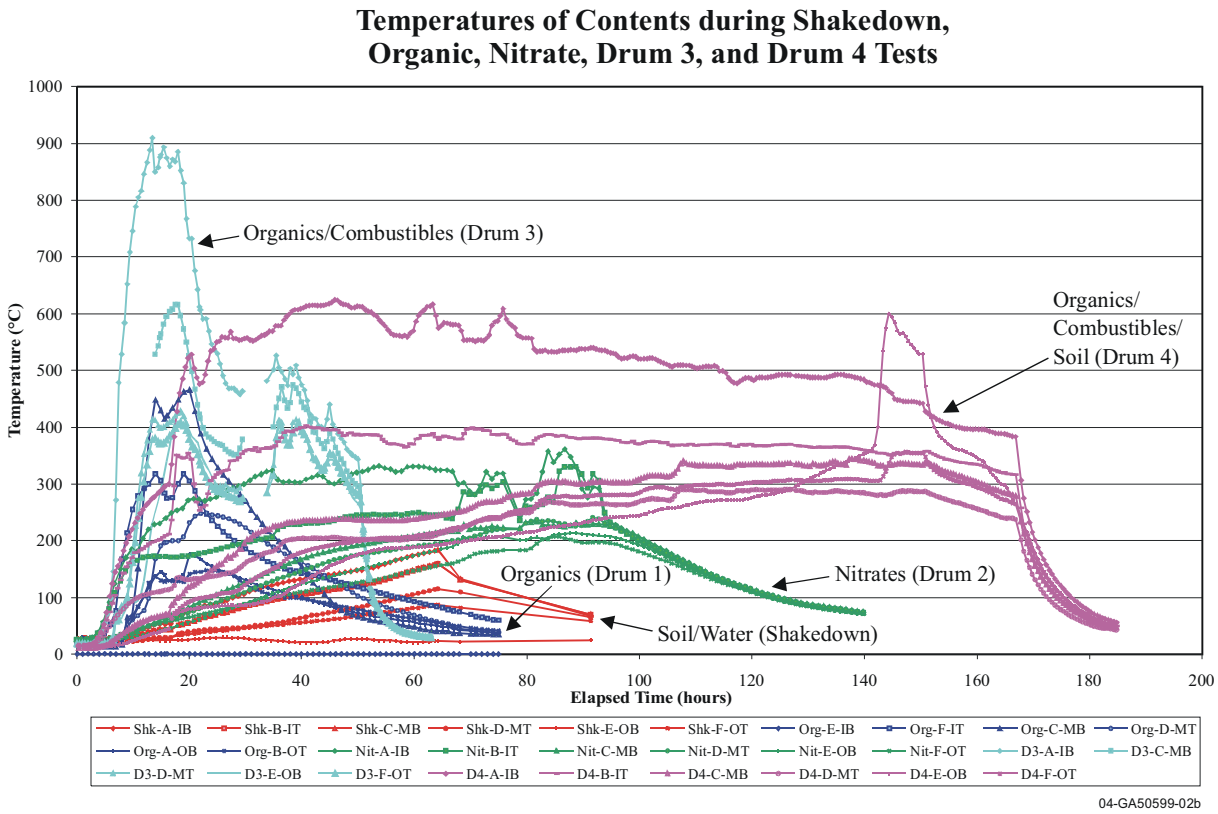

Figure 12. Temperatures of test drum contents.

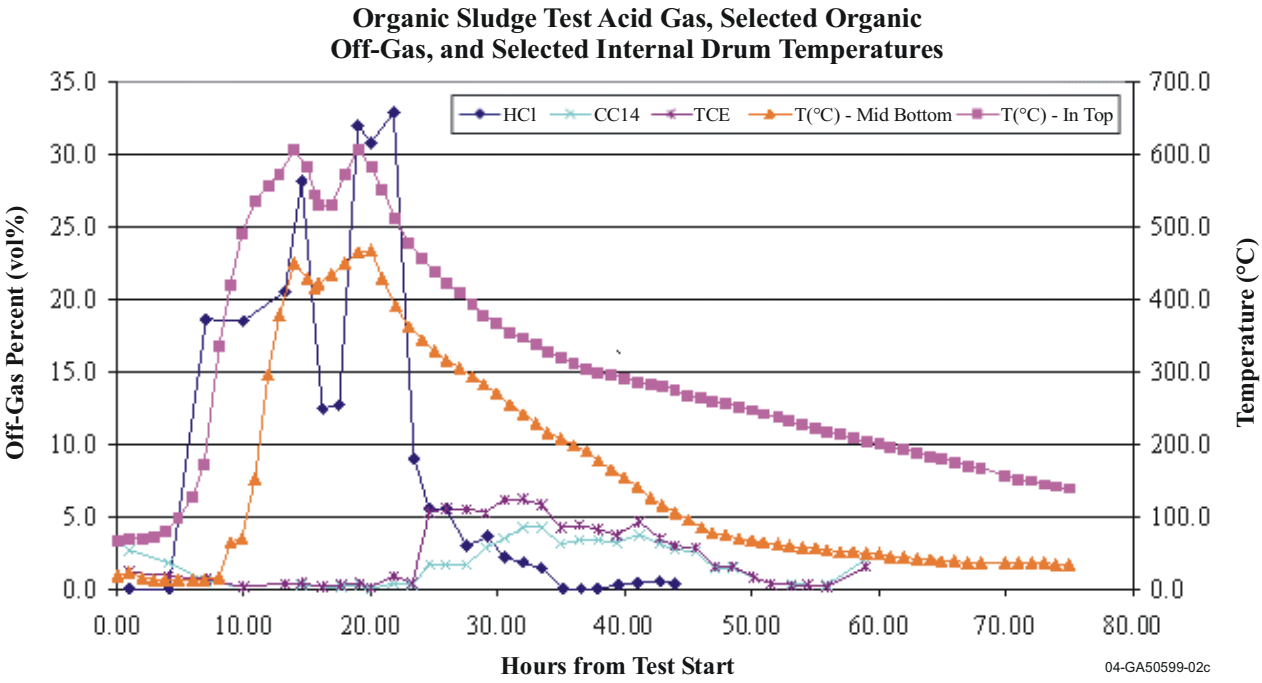

Figure 13. Generation of acid gas in organic sludge test, selected off-gas volatile organics, and selected internal drum temperatures (Drum 1).

The crossover of hydrochloric acid and VOC concentrations apparently was because of incomplete combustion of VOCs volatilized from the feed material. While power was supplied to the heater, the VOCs, which were the only source of chlorine, were evidently fully oxidized to hydrochloric acid, carbon dioxide, and water. When the heater power was turned off, the VOCs continued to volatilize from the drum; however, the presumed combustion zone near or within the heater assembly was apparently no longer hot enough to oxidize the VOCs. A qualitative organic compound scan of an off-gas sample taken during this cooling period showed numerous partially dechlorinated products of the feed organic VOCs, further suggesting incomplete oxidation of organics after the heater power was turned off.

4.2.1.3 Nitrate Salt Surrogate Test (Drum 2). The nitrate salt surrogate was a mixture of 90 wt% nitrate salts, miscellaneous other salts, 1 wt% ethylenediaminetetraacetic acid (EDTA), and 0.5 wt% ceric oxide (added as a plutonium surrogate); details of the recipe are shown in Table I-4 in Appendix I. (The as-mixed formula was normalized to a total of 100%.) For the nitrate salt test, electrical power was applied to the heater assembly for 65 hours. Nominal airflow into the test drum was 0.23 kg (0.5 lb)/minute.

While the nitrate compounds are strong oxidizers, particularly when heated, the only combustible compound in the mixture was EDTA (at 1 wt%), which provided only a trace of fuel for the nitrate oxidizers. Accordingly, heating this mixture was expected to result in only minimal exothermic reactions. As shown in Figure 12, the heating rate for the nitrate salt drum contents was slightly faster than for the shakedown test and much slower than for the organic sludge surrogate test (Drum 1). For the nitrate salt test, heater power was applied for approximately 65 hours, at which time the temperature of the drum contents peaked at approximately 185°C (365°F). The off-gas was sampled and analyzed for the four VOC compounds of the organic sludge surrogate and for hydrochloric acid/chlorine. As expected, since the feed did not contain VOCs, VOCs were not detected in the off-gas. The feed material contained a relatively minor source of chlorine (3 wt% sodium chloride); however, hydrochloric acid/chlorine also was not detectable in the off-gas, most likely because the temperatures were not sufficient to decompose sodium chloride.

4.2.1.4 Organic Sludge Surrogate with Combustible Debris Test Surrogate (Drum 3). A combustible debris surrogate consisting of 40 wt% cotton rags, 40 wt% paper towels, 10 wt% polyethylene beads, 5 wt% polyvinyl chloride beads, and 5 wt% acrylonitrile-butadiene-styrenes plastic beads was prepared for this test (for additional detail, see Table I-5 in Appendix I). The feed formulation for this test consisted of 35 wt% organic sludge, 55 wt% combustible debris, and 10 wt% water. This formulation was intended to simulate the contents of drums buried at the RWMC that contain cutting oil, halogenated solvents, adsorbents, paper, cloth, and plastic scrap. For the organic sludge with combustible debris test (Drum 3), electrical power was applied to the heater assembly for 50.1 hours. Nominal airflow to the test drum was 0.23 kg (0.5 lb)/minute.

As shown in Figure 12, the peak temperature for the organic sludge with combustible debris drum contents was 910°C (1,670°F), observed at 13.5 hours from the start of heating at the inner bottom thermocouple. Peak temperatures and times for the middle and outer thermocouples were 617°C (1,142.6°F) at 18 hours and 423°C (793.4°F) at 18.5 hours, respectively. Both the rate of temperature rise and the peak temperatures were substantially greater than the tests for shakedown, organic sludge (Drum 1), or nitrate salt (Drum 2). Similarly to the organic sludge test, the rapid rise in temperature apparently was because of combustion of the drum contents.

The Drum 3 organics with combustibles feedstock included the organic sludge surrogate (with halogenated solvents) at about one-third the concentration of the test of Drum 1 organic sludge. Consequently, the test of Drum 3 would be expected to show a pattern of off-gas hydrochloric acid and volatile organic generation similar to Drum 1. Drum 3 off-gas hydrochloric acid and volatile organics are shown in Figures 14 and 15, respectively.

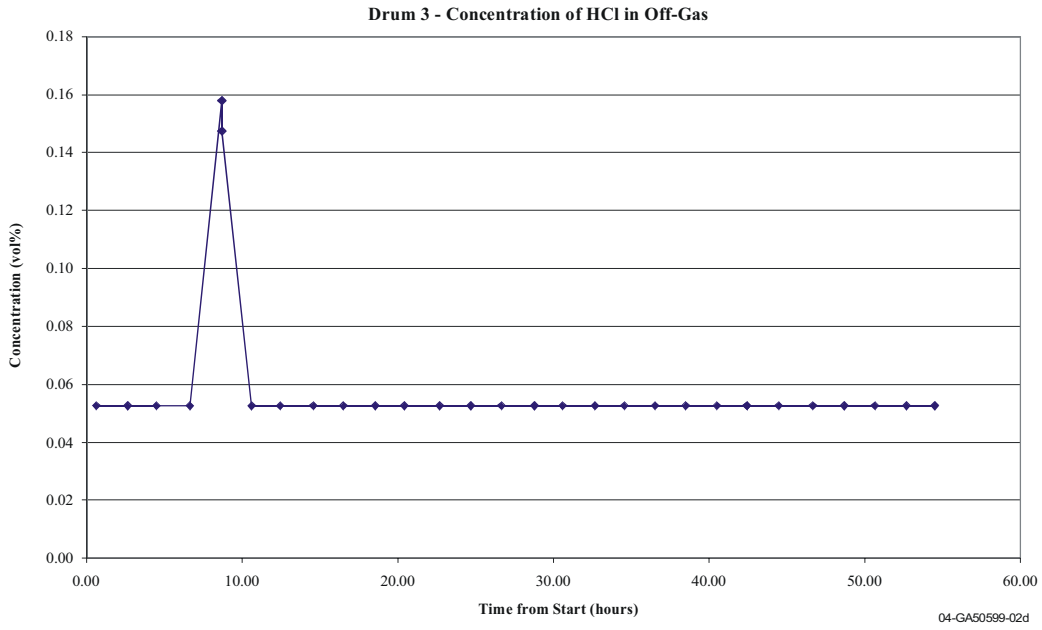

Figure 14. Off-gas hydrochloric acid observed during the test of Drum 3 organic sludge and combustible debris.

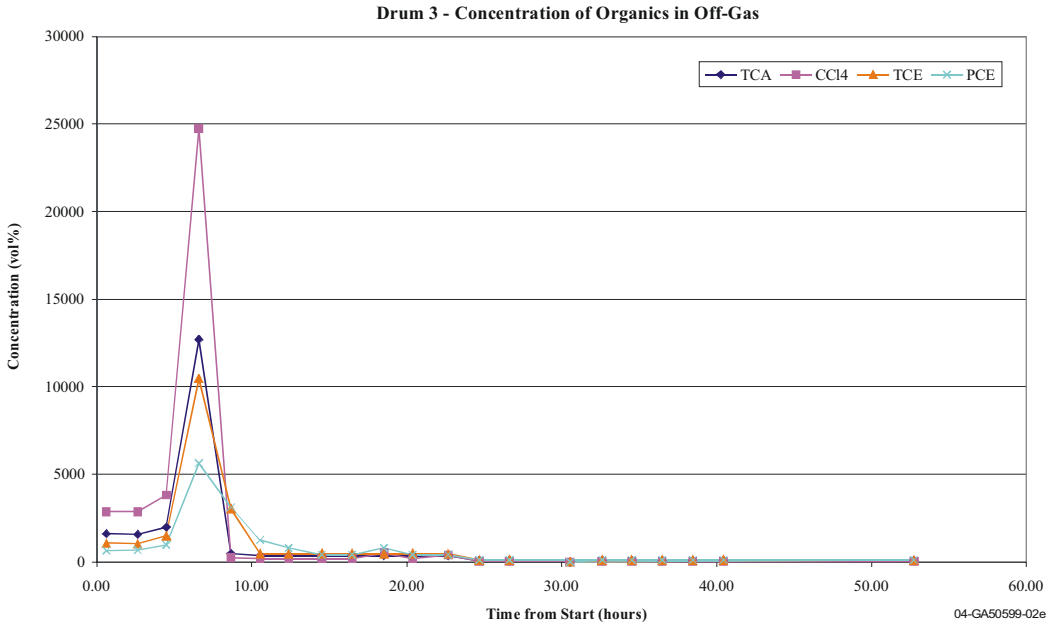

Figure 15. Off-gas volatile organic solvents observed during the test of Drum 3 organic sludge and combustible debris.

Comparison of the Drum 3 results (see Figures 14 and 15) to the Drum 1 results (see Figure 13) indicates much lower off-gas hydrochloric acid and volatile organic concentrations. The Drum 1 results were explained as combustion of halogenated solvents to hydrochloric acid (and carbon dioxide and water) during the early part of the test and volatilization, but poor combustion during the later part of the test. Following this reasoning, the Drum 3 off-gas should show either high concentrations of hydrochloric acid during good combustion or elevated concentrations of volatile organics during poor combustion. Since drum content temperatures were high during the Drum 3 test, the feed halogenated solvents must have volatilized, raising the question of what happened to the chlorine in the halogenated solvents. It appears to have neither burned to hydrochloric acid nor come off unaltered as volatile organics.

Possible alternative fates of feed chlorine are that hydrochloric acid was scrubbed by feed constituents, which seems unlikely since there were no alkaline components in the Drum 3 feedstock or that the halogenated solvents partially pyrolyzed, and the chlorine in the halogenated solvents came off as chlorinated organic combustion products. Rapid heating of the Drum 3 contents may have resulted in incomplete combustion, or the rapid heating and associated evident burning of combustible debris may have caused an off-gas dilution effect caused by rapid generation of large volumes of off-gas.

4.2.1.5 Organic Sludge Surrogate with Combustible Debris and Soil Surrogates Test (Drum 4). A soil surrogate—containing a tracer—consisting of 83 wt% soil from the INL Site, 15 wt% water, and 2 wt% ceric oxide was prepared for this test (additional detail is provided in Table I-6 of Appendix I). The feed formulation for this test consisted of 40 wt% organic sludge, 30 wt% tracer containing soil, and 30 wt% combustible debris. This formula simulated the contents of drums buried at the RWMC mixed with soil from the INL Site. For the organic sludge with combustible debris and soil test (Drum 4), electrical power was applied to the heater assembly for 167 hours. Nominal airflow to the test drum was 0.23 kg (0.5 lb)/minute.

As shown in Figure 12, the peak temperature for the drum contents was 619°C (1,146ºF), observed at 46.8 hours from the start of heating at the inner bottom thermocouple. Peak temperatures and times for the middle and outer thermocouples were 344°C (686ºF) at 138 hours at the middle bottom thermocouple and 600°C (1,112ºF) at 144 hours at the outer bottom thermocouple. Note that the outer bottom thermocouple, and to a lesser extent the outer top thermocouple, showed a spike in temperature near the end of the test. During most of the test, the outer bottom thermocouple registered the lowest temperature of all the drum content thermocouples, as would be expected. However, for approximately 10 hours near the end of the test, the outer bottom thermocouple crossed over and registered the highest temperature in the drum during that period and nearly the highest temperature of any thermocouple for the entire test. Assuming that the high temperature reading was not a malfunction, which seems unlikely since the outer top thermocouple also registered a temperature rise during the same period, the only apparent cause of the temperature spike would have been delayed burnout of drum contents near the outside of the drum.

The peak temperatures for the Drum 4 (see Figure 12) test were greater than for the tests for shakedown, organic sludge (Drum 1), or nitrate salt (Drum 2) but less than the test of Drum 3 organic sludge with combustible debris. With the exception of the outer thermocouple temperature spike near the end of the test, the general rate of temperature rise for Drum 4 was less than that observed for all but the shakedown test.

Drum 4 off-gas hydrochloric acid and off-gas halogenated organics are shown in Figures 16 and 17. Comparison of results from Drum 1 (see Figure 13), Drum 3 (see Figures 14 and 15), and Drum 4 shows a closely similar pattern of off-gas hydrochloric acid and halogenated organic evolution for Drum 3 and Drum 4 tests, with both differing substantially from Drum 1, which showed much higher concentrations of off-gas hydrochloric acid and off-gas halogenated organics. The peak hydrochloric acid and halogenated organic concentrations for Drum 4 occurred between 15 and 20 hours from the start of

the test, while peak concentrations for Drum 3 were between 5 and 10 hours from the start of the test. This appears to be consistent with the slower heatup rate for Drum 4, which was expected because of the lower fuel content for Drum 4 feedstock.

Posttest analysis of Drum 4 contents showed very low concentrations of residual halogenated organic feed constituents, generally undetectable, and less than 1 mg/kg in all instances.

Paralleling the discussion of the Drum 3 test results above, the lower concentrations of off-gas hydrochloric acid and halogenated organics for Drum 4 relative to Drum 1 may have been caused by evolution of chlorinated organic pyrolysis products of the Drum 4 feed constituents. To assess this possibility, several off-gas samples from Drum 4 were analyzed using complete mass spectral scans of the sample gas chromatograms. Complete mass spectral scans can reveal and tentatively identify miscellaneous organic compounds in the analysis sample. In this case, analysis of Sample 10, which was taken 16.7 hours from the start of the test, showed relatively high concentrations of partial decomposition products, including benzene, styrene, and several chlorinated organic compounds. Generated over the entire test period, the Drum 4 chlorinated decomposition products might have accounted for the bulk of the chlorine present in the Drum 4 feedstock.

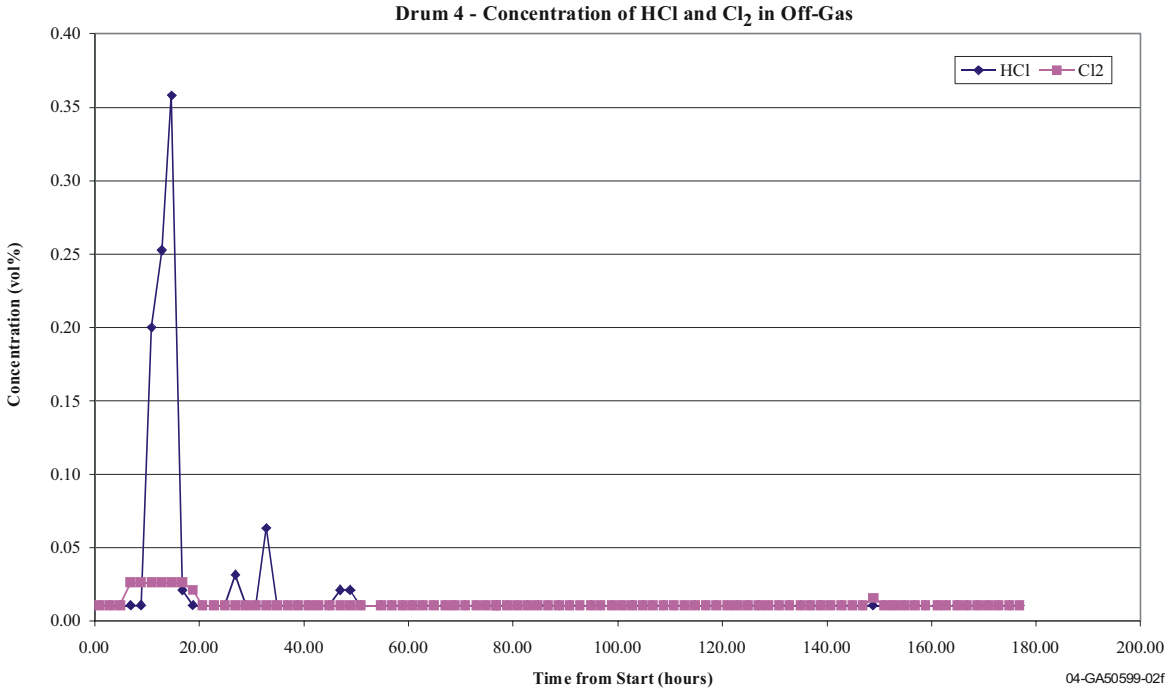

Figure 16. Off-gas hydrochloric acid observed during the test of Drum 4 organic sludge with combustible debris and soil.

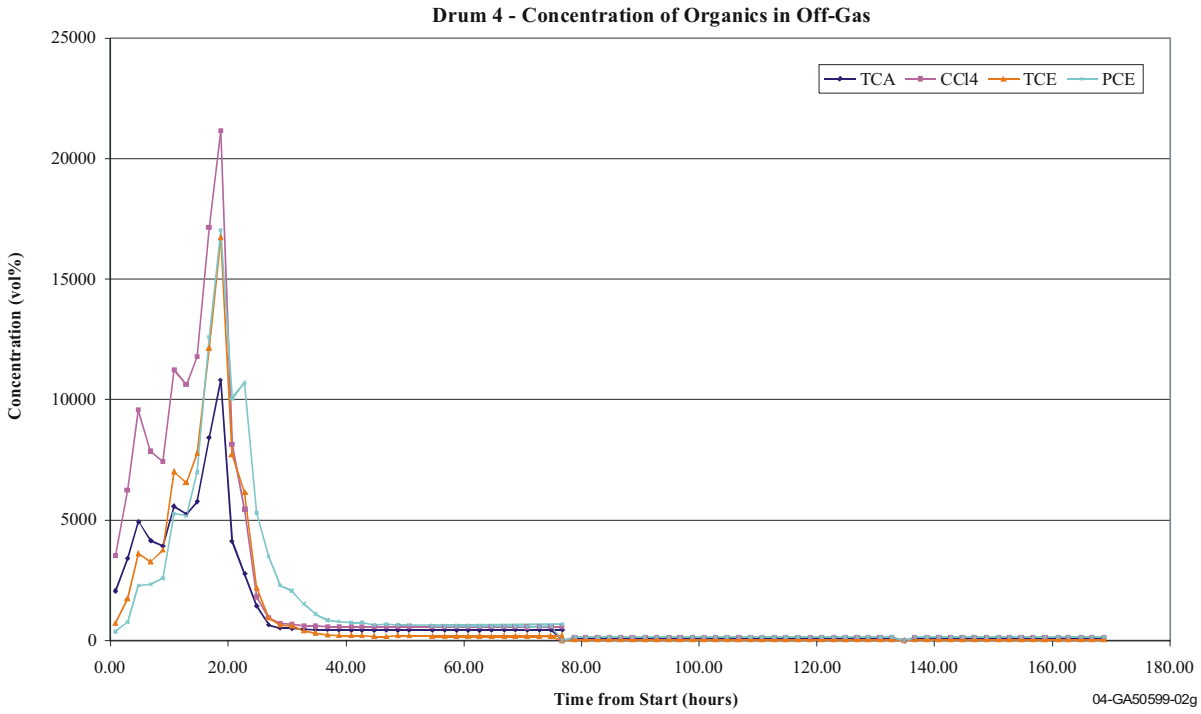

Figure 17. Off-gas volatile organic solvents observed during the test of Drum 4 organic sludge with combustible debris and soil.

4.2.1.6 Conclusions from MSE Drum Tests. Based on MSE tests, oxidation of subsurface materials should be expected if oxygen is present during ISTD. The location and completeness of the oxidation will depend on amount of oxygen present, temperature, and location of oxygen and materials being oxidized. The MSE tests also indicate the potential for chlorinated organic compounds to be released during ISTD. These chlorinated compounds can be readily managed by an off-gas treatment system similar to those regularly employed where ISTD is used to treat organic compounds.

The feedstocks containing significant quantities of combustible materials were essentially self-heating after an initial heatup period, provided that combustion air was supplied to the test drum. The self-heating of combustible drum contents appeared to produce gaseous partial-decomposition products, though supplying electrical power to the heater assembly appeared to be necessary for more complete combustion of the gaseous partial-decomposition products. However, the bulk of the heating power for the drum contents came from combustion of drum contents. The rate of heatup of the drum contents corresponded to the relative amount of fuel in the feedstocks. For these tests, the rate of heating increased in the following order: shakedown (soil and water), Drum 2 (nitrate sludge surrogate), Drum 4 (organic sludge, combustible debris, and soil), Drum 1 (organic sludge), and Drum 3 (organic sludge and combustible debris).

Drum 1 (organic sludge), Drum 3 (organic sludge with combustible debris), and Drum 4 (organic sludge with combustible debris and soil) tests used feedstock containing halogenated solvents. In the Drum 1 test, the off-gas initially contained high concentrations of hydrochloric acid and later relatively high concentrations of feedstock halogenated organics. This was attributed to initial complete combustion of halogenated organics to hydrochloric acid, carbon dioxide, and water, followed by a period of obvious noncombustion of volatilized halogenated organics. The noncombustion of halogenated

organics was apparently caused by removing electrical power from the heater assembly and discontinuing combustion air to the drum, which was done in order to stop the test.

The MSE concluded that the heater assembly performed as expected, gradually heating surrogates of buried organic sludge, nitrate salts, organic sludge with combustible debris, and organic sludge with combustible debris and soil. Heating feedstocks containing halogenated organics resulted in emission of hydrochloric acid, chlorinated decomposition products, and unaltered feed organics, indicating a need for downstream off-gas treatment of buried waste containing high concentrations of organic constituents.

A secondary conclusion was that organic sludge, nitrate salts, and organic sludge with combustible debris could be tested safely in the drum-scale test bed and ultimately treated in this manner in the field. Mixtures of organic sludge or combustible debris with nitrate salts, a combination of fuel and oxidizer, were not tested. Fuel with oxidizer mixtures of this type was tested at the Energetic Materials Research and Testing Center in New Mexico. The results of those tests are reported separately in Section 4.4 and Appendix J of this report.

The results from this test show that heating the waste removes some contaminants from the waste, in particular, the organic fraction and, in some cases, nitrate salts from the waste as long as the temperatures and airflow are controlled. It will be necessary to provide an off-gas treatment system to ensure that contaminants are not released into the atmosphere.

4.2.2 Off-Gas, Bench-Scale Filter, and Mass Balance Analysis during ISTD of Transuranic Surrogates and Waste

These bench-scale tests were conducted using a tube furnace (see Appendixes K and L for a description of the procedures and apparatus).

4.2.2.1 Off-Gas. Grab samples of the off-gas stream were taken periodically (generally at zero, one, and three hours) during ISTD of the organic sludge surrogate, organic sludge waste, and Pad A nitrate salts from a septum port on the line between the filter and the bubbler. These samples were analyzed by gas chromatography-electron capture detector for organochlorine constituents and compared with a carbon tetrachloride gas standard. A split also was analyzed by thermal conductivity detector for carbon monoxide, carbon dioxide, nitrous oxide, and sulfur dioxide. The results are summarized below; the values of individual measurements are provided in Table L-10 of Appendix L.

Organochlorine constituents were analyzed using an electron capture detector. The electron capture detector was calibrated using carbon tetrachloride, and in fact, carbon tetrachloride was detected at very low concentrations (part-per-billion levels) in the off-gas as shown in Figure 18. No significant amounts of carbon tetrachloride were found in the off-gas from the organic sludge waste samples (see Figure 19). Examination of Pad A carbon tetrachloride data in Figure 20 unexpectedly shows small amounts of carbon tetrachloride. Therefore, the carbon tetrachloride concentrations reported here for both waste types may be from residual carbon tetrachloride in the system and not from the samples.

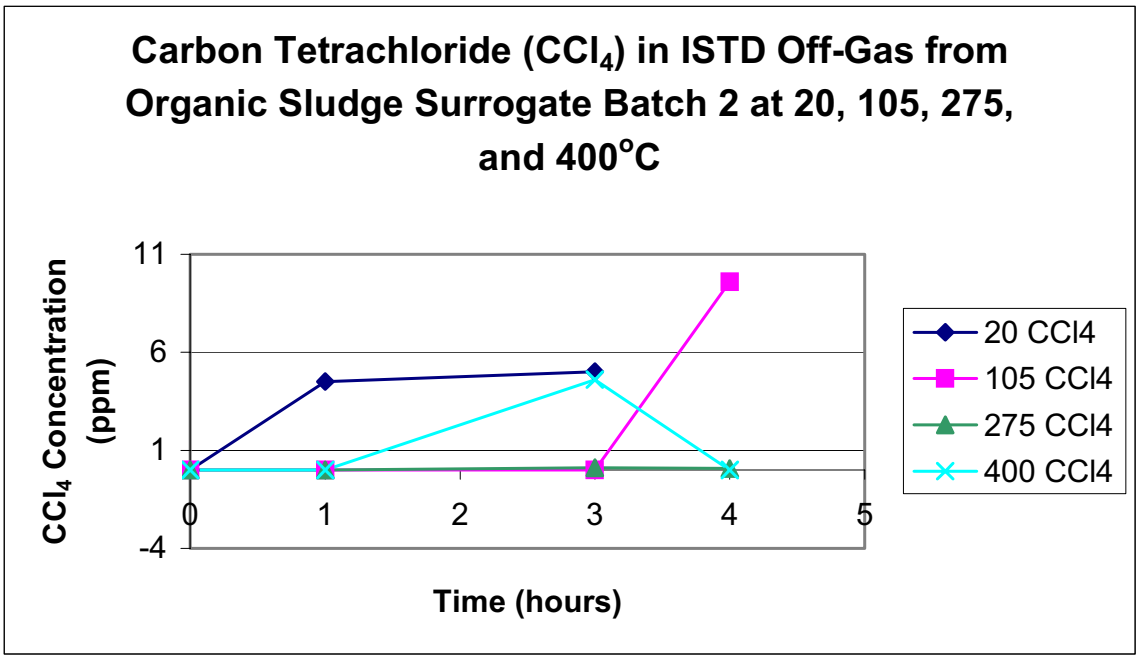

Figure 18. Carbon tetrachloride concentration in off-gas from ISTD as a function of time and temperature for samples of organic sludge surrogate.

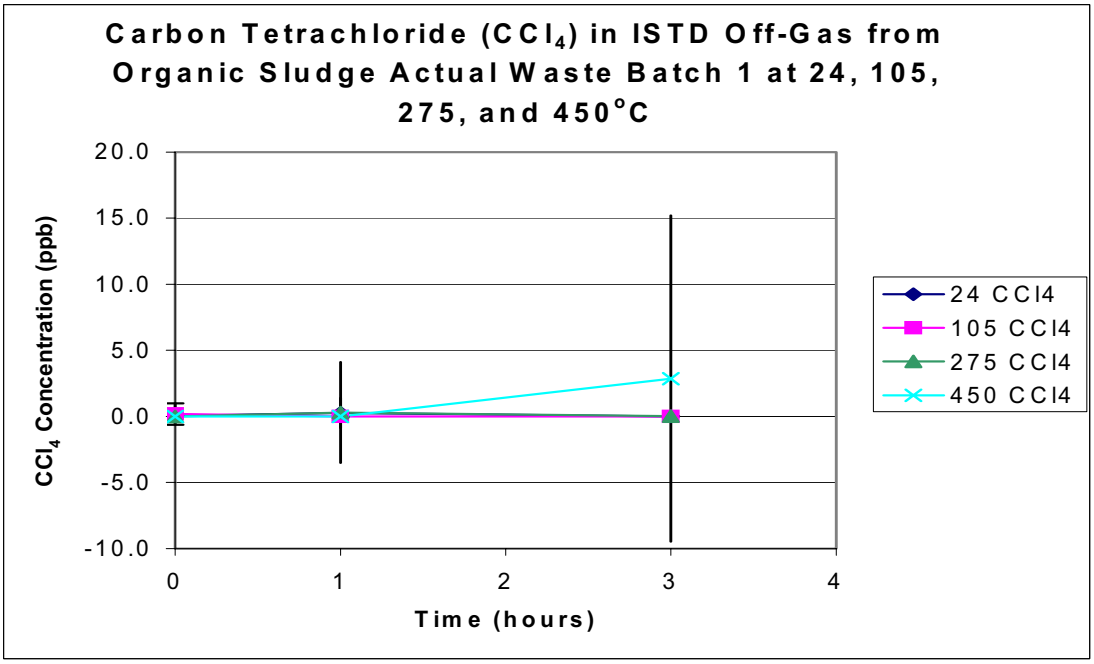

Figure 19. Carbon tetrachloride concentration in off-gas from ISTD as a function of time and temperature for samples of organic sludge waste.

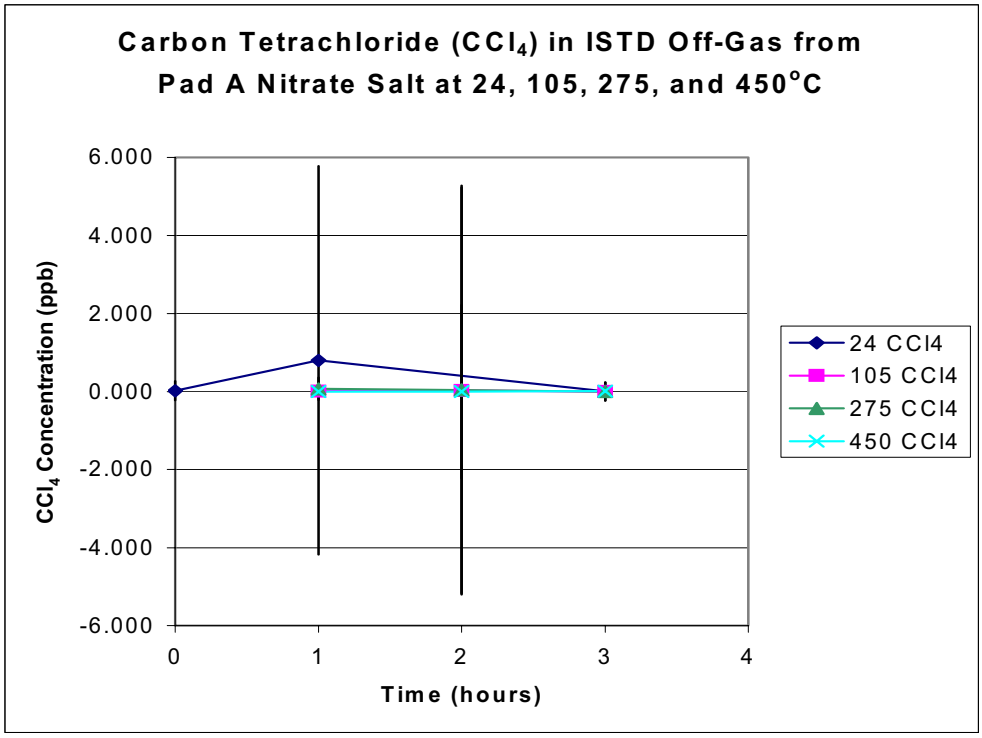

Figure 20. Carbon tetrachloride concentration in off-gas from ISTD as a function of time and temperature for samples of Pad A nitrate salt.

Further evidence of this is that no predictable sequence of carbon tetrachloride evolution occurs with time as measurements were made immediately upon achieving temperature for a run (1 hour into the run and 3 hours into the run). This experimental setup may not have been adequate for collecting desired off-gas data.

The carbon monoxide, carbon dioxide, nitrous oxide, and sulfur dioxide were analyzed using a thermal conductivity detector. Similar problems in experimental design affected quantification of these analytes. In general, no nitrous oxide, carbon monoxide, or sulfur dioxide was detectable in the off-gas of the sludge surrogate (see Figure 21 [only one sample; therefore, no confidence intervals]) and Pad A nitrate salt (see Figure 22) samples, with occasional and apparently random exceptions for the sludge. Results were similar in the organic sludge waste to the organic sludge surrogate. Only carbon dioxide was routinely detectable, with most samples showing a baseline amount probably from carbon dioxide in the air used as carrier gas. Pure air injections result in similar responses. For more detailed information, see Appendix L.

Figure 23 shows a summary of the bubbler water analytical results for nitrite and nitrate in off-gas from Pad A salt ISTD and organic sludge waste composite ISTD. Bubbler volume was 100 mL (3.4 oz) initially, made slightly basic with sodium hydroxide. These measurements were made by ion chromatography using an ion chromatograph (Dionex 2000i) with carbonate/bicarbonate eluent and a sulfuric acid suppressor column. No pattern is discernable in the results, and surprisingly, organic sludge waste composite off-gas contained more measurable nitrate than did the Pad A salt. The source of this nitrate is unknown but may be related to system contamination, as previously discussed.

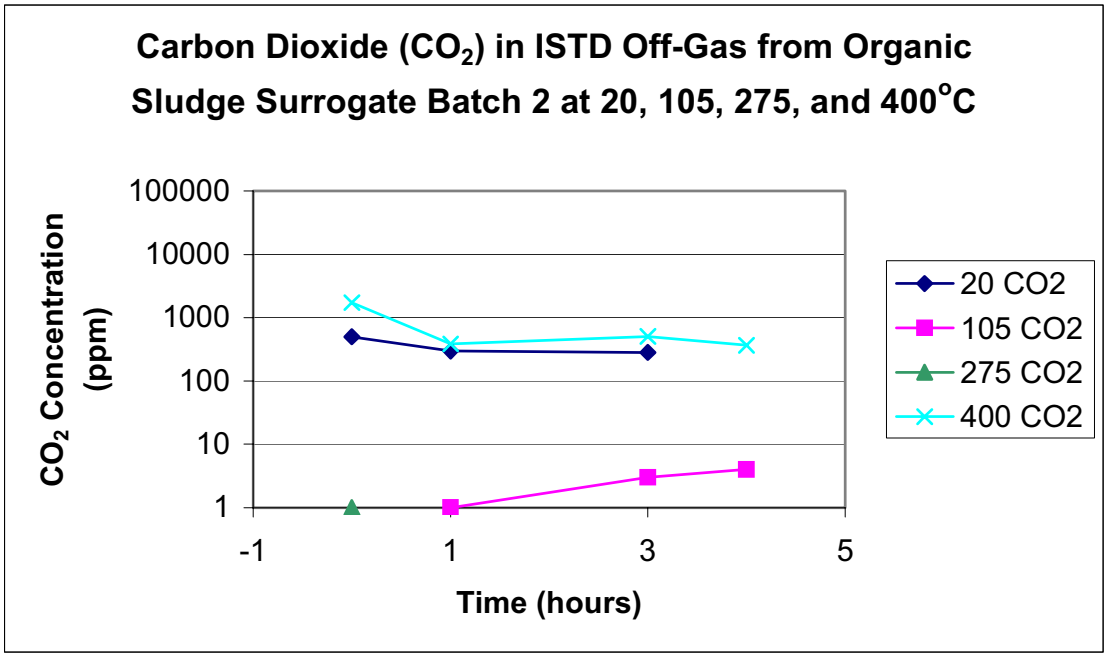

Figure 21. Carbon dioxide concentration in off-gas from ISTD as a function of time and temperature for samples of organic sludge surrogate.

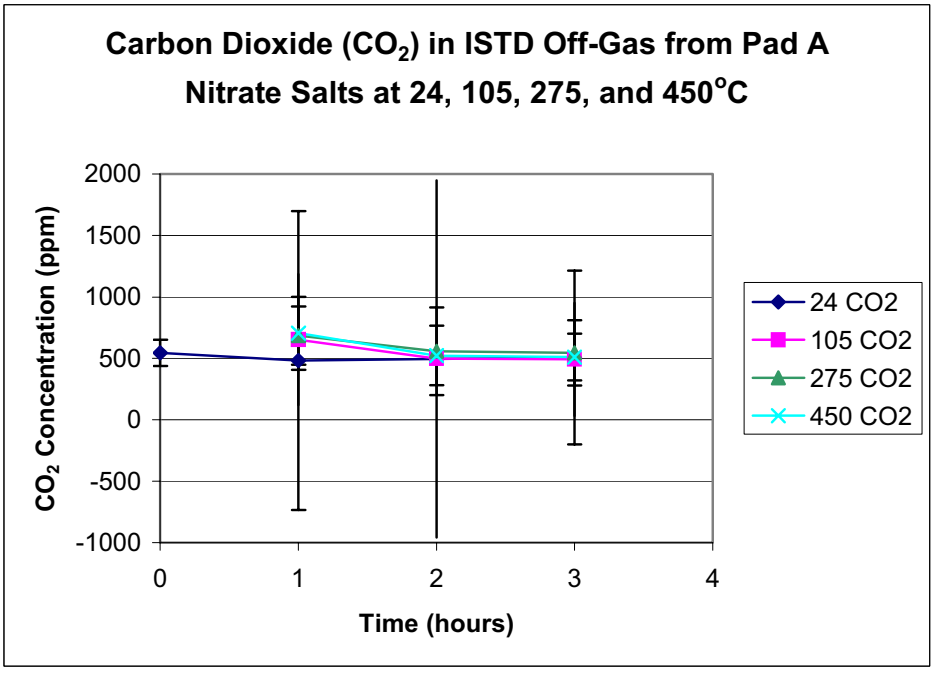

Figure 22. Carbon dioxide concentration in off-gas from ISTD as a function of time and temperature for samples of Pad A nitrate salt.

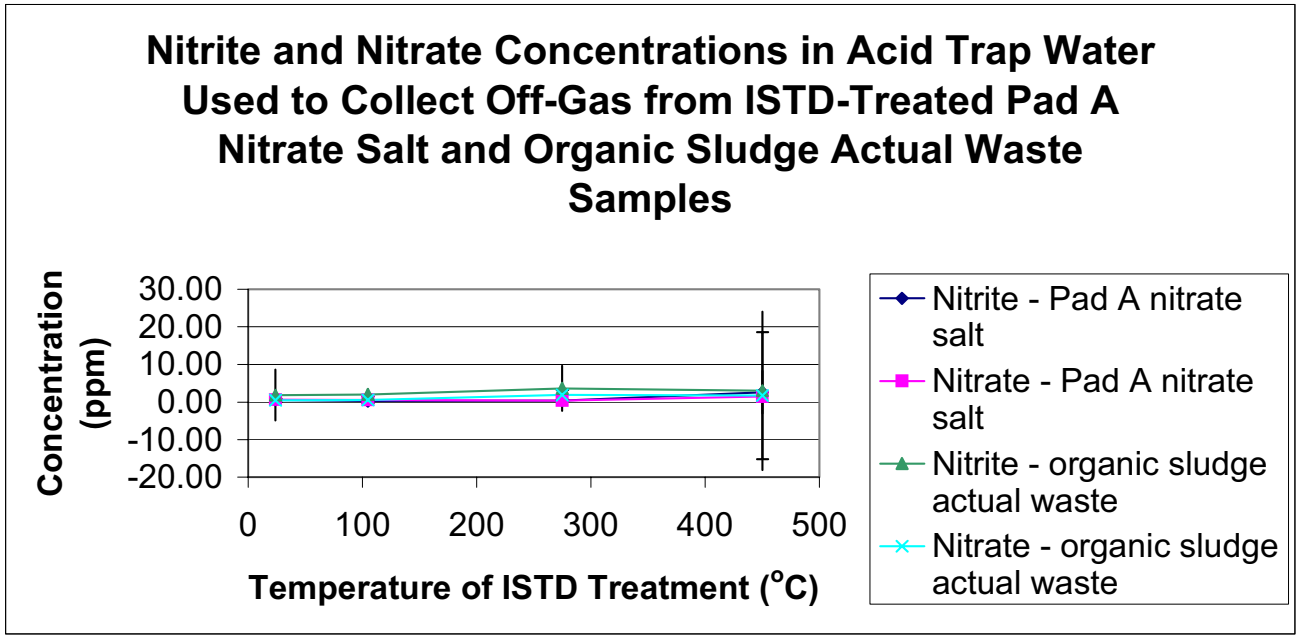

Figure 23. Nitrite and nitrate concentrations from off-gas in acid trap water for ISTD-treated samples of Pad A nitrate salts and organic sludge waste.

4.2.2.2 Filter. A 0.2-µm filter was placed in the off-gas stream to collect any radionuclide particulates released during ISTD treatment. The results were different than expected but not conclusive. The filters in the off-gas stream contained uranium during ISTD for soil (see Figure 24), inorganic sludge surrogate (see Figure 25), organic sludge surrogate (see Figure 26), organic sludge waste (see Figure 27), and Pad A nitrate salt waste (see Figure 28). For Figures 24 through 28, 95% confidence intervals are shown; some data points were below detection limits (see Table L-2 in Appendix L). The filters for organic sludge surrogate and organic sludge waste contained uranium and plutonium. Most of the measurements of filters did not detect measurable quantities (green shading on Table L-2 in Appendix L) of neptunium, americium, and plutonium. No trend in uranium was present on the filter with temperature. Also, the standard deviations and 95% confidence intervals for uranium and plutonium were generally of the same order of magnitude as the mean for uranium and plutonium, meaning that there was a lot of variability in the data and that it should be used more as qualitative rather than quantitative data.

4.2.2.3 Mass Balance. Weight loss was measured for samples treated with ISTD. The weight loss data are summarized in Figure 29 (values of individual measurements are provided in Table L-8 in Appendix L). All of the samples were heated for a 4-hour time period. As expected, the soil and Pad A nitrate salt samples showed the smallest (less than 10 wt%) change in mass on heating. These materials contain minimal amounts of organic compounds and water. The inorganic sludge surrogate samples lost about 25% of their original mass. Most of the mass loss occurred at 105°C (221°F); this is not surprising since the material contained no organics and approximately 20 wt% water. The organic sludge surrogate contained approximately 50 wt% VOCs and 29 wt% Texaco Regal Oil. Overall, the organic sludge surrogate lost more than 60% of its mass, but not until 275°C (527°F). Surprisingly, given the large percentage of volatile organics in the material, only 5% of the initial mass was lost at 105°C (221°F). Mass loss above 50% may represent loss of the more volatile elements of Texaco Regal Oil.

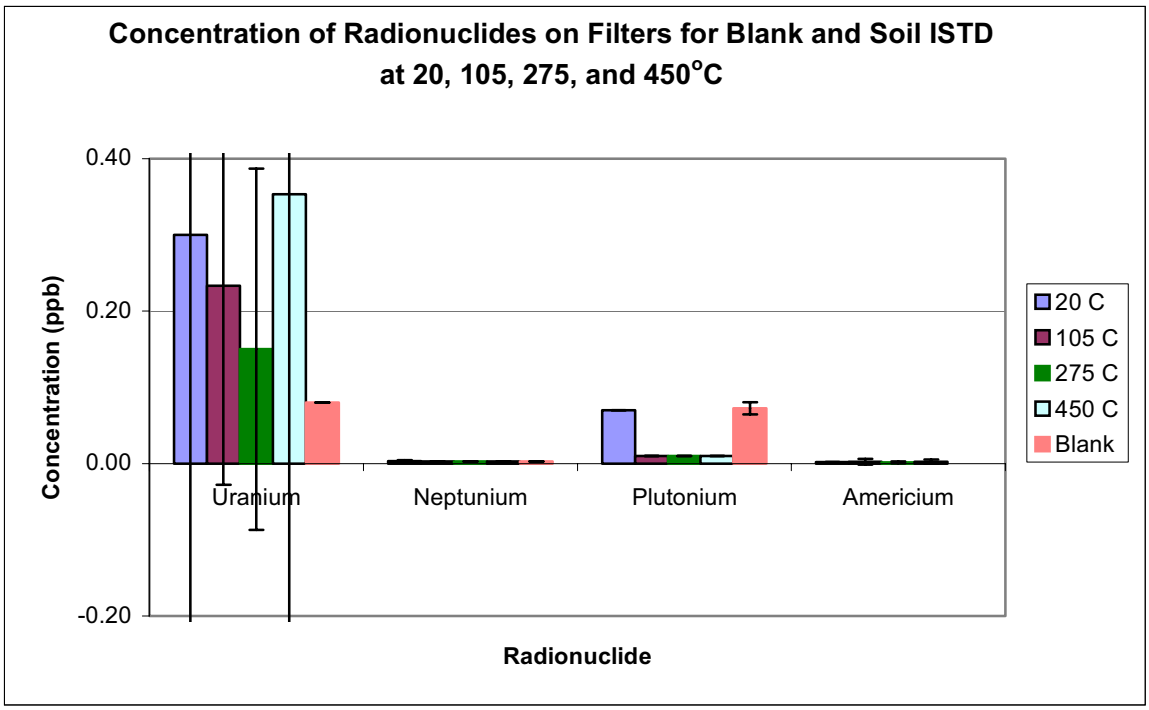

Figure 24. Concentrations of radionuclides on blank and soil ISTD filters.

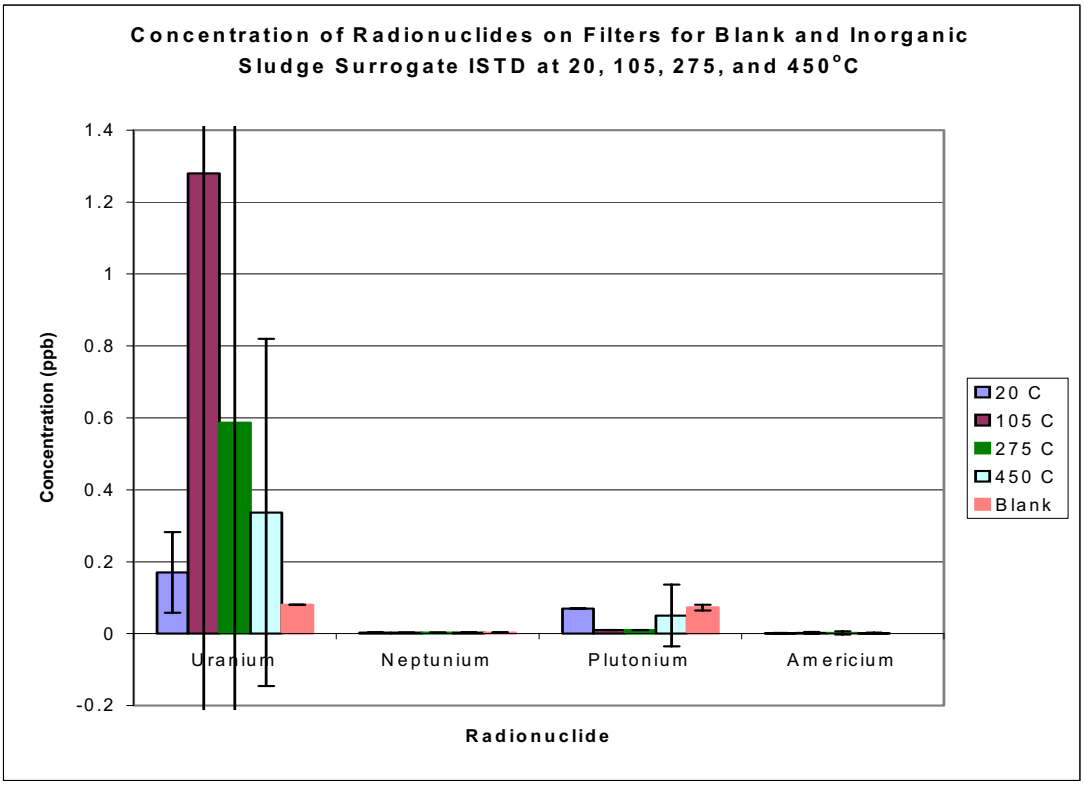

Figure 25. Concentrations of radionuclides on blank and inorganic sludge surrogate ISTD filters.

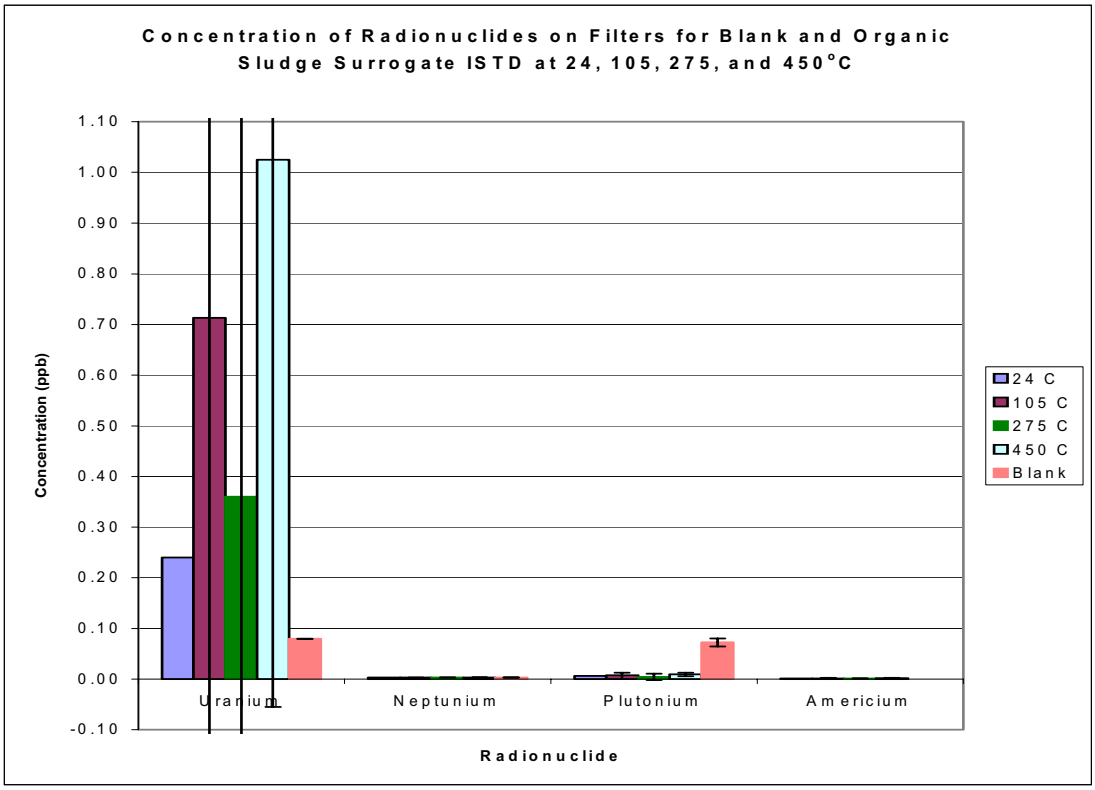

Figure 26. Concentrations of radionuclides on blank and organic sludge surrogate ISTD filters.

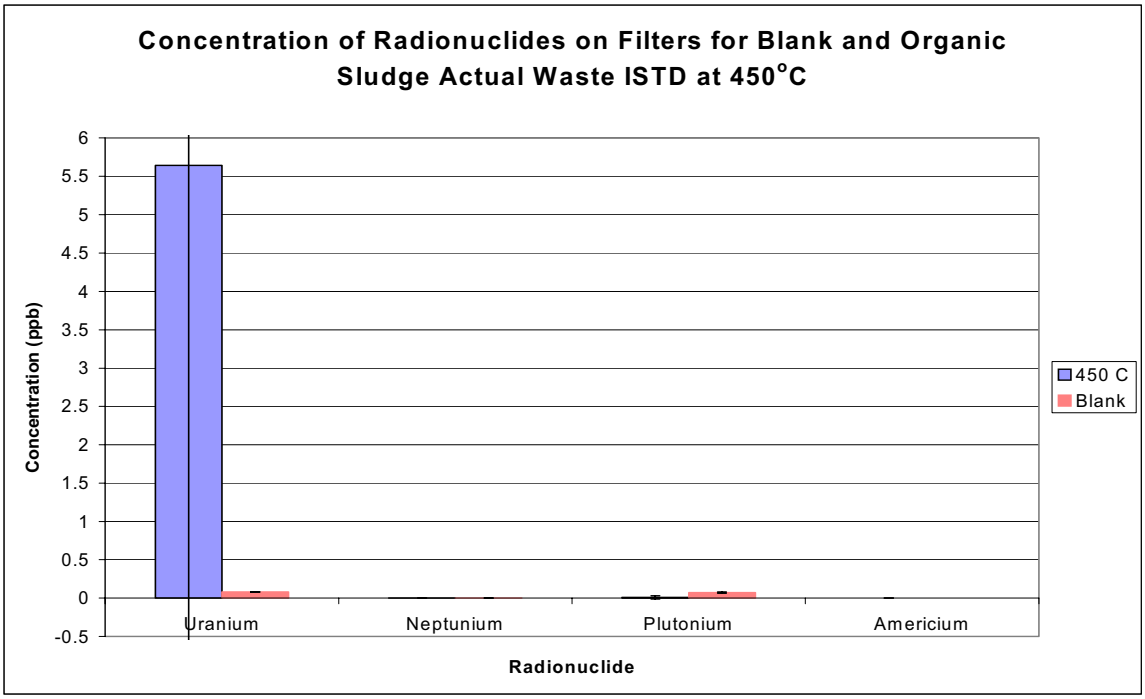

Figure 27. Concentrations of radionuclides on blank and organic sludge waste ISTD filters.

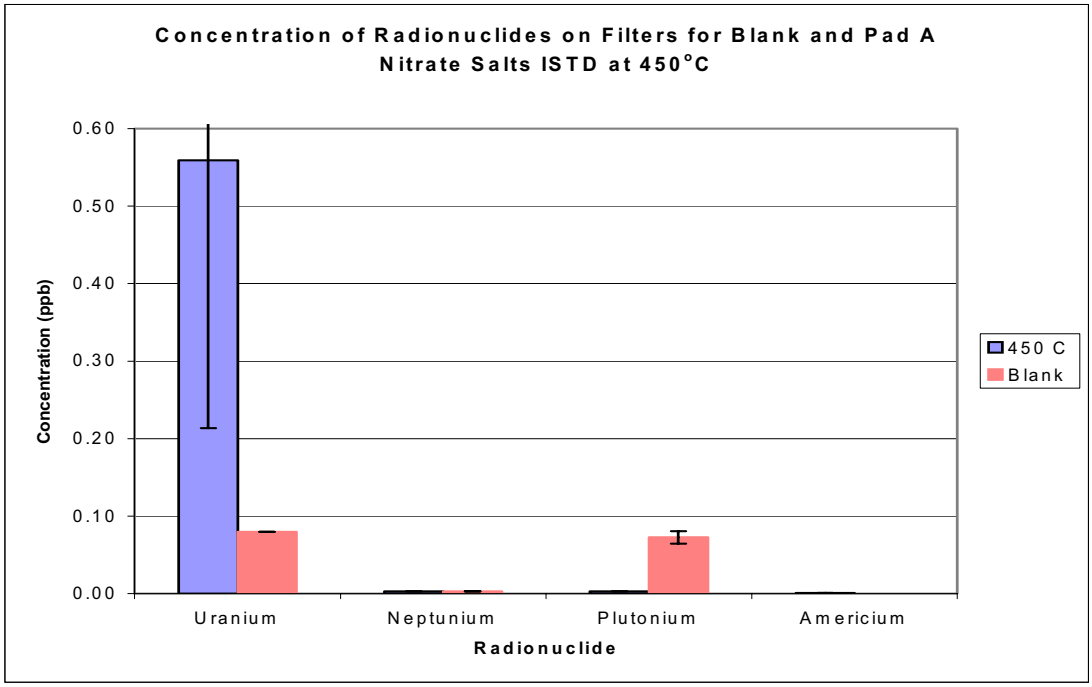

Figure 28. Concentrations of radionuclides on blank and Pad A waste ISTD filters.

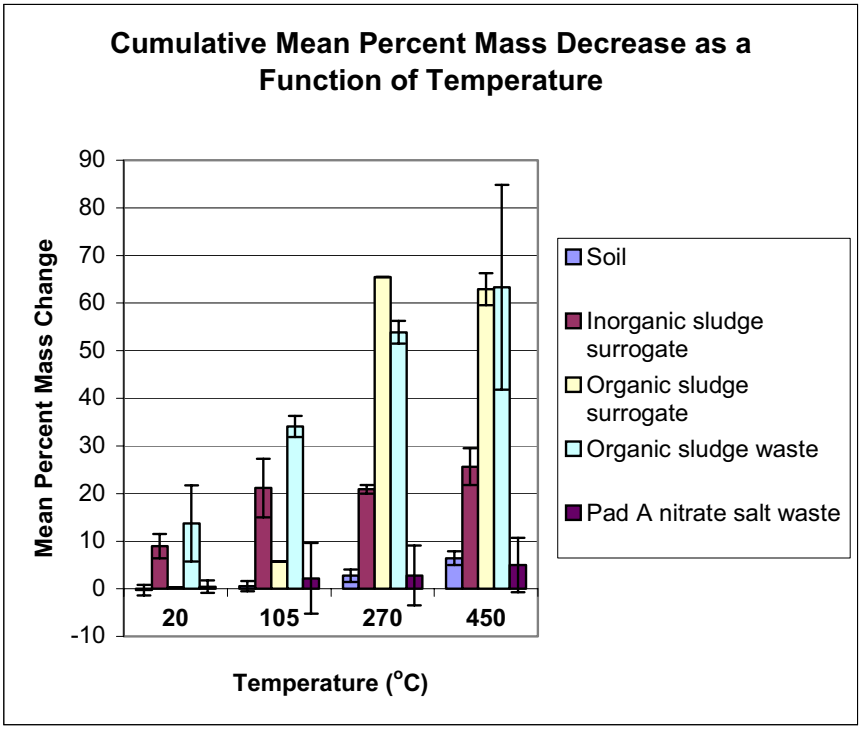

Figure 29. Cumulative mean percent mass change as a function of temperature and a duration of four hours.

Compositional analyses (radionuclide and organic compounds) for two separately prepared batches of organic sludge waste composite are shown in Table L-3 in Appendix L.

The concentration of radionuclides in each sample was measured before and after ISTD treatment. The expected concentrations of radionuclides in samples after heating were calculated based on the mean measured mass losses of samples of the material and the assumption that no radionuclides were released from the sample during heating. The results are presented in Table L-4 in Appendix L. No data were available on inorganic sludge surrogate. The data for organic sludge waste and one of the organic sludge surrogate batches suggest that americium was lost during heating, but not uranium. The data for the Pad A waste suggest that uranium and plutonium were lost during heating. Overall, the data showed considerable variation. In several cases, the measured concentration of radionuclides was greater than the expected concentration. This difference could be caused by the difference between the actual mass loss in the measured sample and the average mass loss used to calculate the expected concentration or errors in the measured concentration of radionuclides.

Table L-4 in Appendix L shows that the mean actinide concentrations increased by a factor of 1.5 to 2.5 in the posttreatment organic sludge waste composite, caused by the 50 to 60% mass loss characteristic of treated organic sludge. The possible exception was americium, which apparently decreased in concentration following heat treatment in the second trial; however, americium was not detectable on gas stream filters (see Figures 26 and 27) or in the bubbler solution. The mean concentration of uranium decreased substantially in posttreatment Pad A salt. This uranium also did not appear on the filter downstream of the heated sample or in the bubbler solution, and thus, it must be hypothesized that the uranium, americium, or both plated out on the quartz tubing immediately outside the furnace before reaching the filter. Although it was heat taped, visual amounts of organic material also plated there.

In conclusion, the filter and composition data are not consistent with respect to release of radionuclides during ISTD. Uranium and plutonium are seen on the filters for several waste materials, while americium apparently decreased in organic sludge surrogate and waste samples during heating. In all cases, the 95% confidence intervals are the same order of magnitude or larger than the mean values. Given the inconsistent picture presented by the data, conclusions about the fate of radionuclides during ISTD treatment cannot be made. Additional testing and controls (including a detailed full mass balance) would be necessary to confirm the extent of potential radionuclide release during ISTD.

4.3 Determine the Degree of Hazardous Organic Contaminant and Nitrate Removal or Destruction from Soil and Waste

In situ thermal desorption can remove organic compounds from the waste. Lower temperatures (100 to 200°C [212 to 392°F]) are appropriate for removing VOCs and water; this is the temperature range of interest for the SDA. Higher treatment-zone temperatures (above 200°C [392°F]) are used for removing and destroying semivolatile compounds. Treatment-zone temperatures of 400 to 500°C (752 to 932°F) have been used to remove and destroy polychlorinated biphenyls at some field sites (TerraTherm 2005b; TerraTherm 2005c; U.S. Navy 1997). The removal will be a combination of vaporization and thermal destruction, depending on the temperature, materials, and oxygen present. Section 4.3.1 covers work completed by MSE on nonradioactive surrogates. The MSE tests were larger drum-scale tests. Section 4.3.2 covers ISTD of radioactive surrogate and waste completed at the INL Site, and was performed on a smaller scale using surrogate and waste that was ISTD treated. The second set of tests was used to confirm that the MSE drum-scale tests matched what would occur using the radioactive waste and surrogate.